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Phototropism*

(Photochromism)

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1 INTRODUCTION

Marckwald¹ gave the name "phototropy" to the phenomenon in which a solid changes colour when exposed to light but reverts to its original colour in the dark. The term "phototropy" is not a particularly good one to explain this phenomenon of colour change of solids and solutions since it has been used by botanists, biologists and biochemists for many years to describe a true tropistic behaviour in plants; also the form of the word does not suggest to the English-speaking scientist that it is a phenomenon rather than a field of knowledge. Couch² recommended that people in the biological fields drop the use of the term phototropy as related to plants and leave the term for photochemists. However, his recommendation has not been accepted by either group of workers and the term is still used by both to mean different things. The authors of this review have chosen to use the term "phototropism" as the title for this review since the term implies a phenomenon, and secondly, the term is well established in the literature. In recent years the term "photochromism" has been rather widely used in chemical literature to characterize those systems, solids and solutions, which undergo a colour transformation in the visible region when the systems are exposed to an exciting radiation. The term photochromism is descriptive of the phenomenon taking place and because of its current usage

* This review is an outgrowth of work initiated with one of us (G.H.B.) by the Aerospace Medical Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

has been used as the sub-title of this review.

Four reviews in the different areas of phototropy have been published. Stobbe³ reviewed the field as related to chemistry up to about 1921, Chalkley⁴ reviewed the same field up to about 1928, Bhatnagar, Kapur, and Hashmi⁵ reviewed the field up to about 1938, while Van Overbeek⁶ reviewed the biological field up to about 1938. The present article covers the literature reviewed by *Chemical Abstracts* up to 1959 of this publication, with some references to work of a later date. It is difficult to cover all articles containing information on phototropism since the information may be buried in an article as secondary to the main content. Only those systems which show reversibility of colour change have been described; a one-way colour change has not been considered since such a change is not a true example of phototropism.

ter Meer⁷ appears to have been the first person to observe a phototropic colour change when he exposed the potassium salt of dinitroethane to exciting radiation. Another contribution to the study of phototropism was published in 1881 by Phipson⁸ who had the strange case of a painted gate post that changed colour called to his attention by a friend, Thomas Griffiths. Phipson⁹ made many qualitative tests on the paint pigment now called "lithopone", which had been used to paint this gate post. He speculated about the cause of phototropy, which he called the "actinic phenomenon", but was not able to reach a definite conclusion about it. It should be noted in passing that the colour change exhibited by lithopone was probably first observed about 1870¹⁰. Cawley¹¹ discussed his experiences with lithopone and pointed out that he could make a preparation of the pigment which would be stable to light by adding about three per cent of ammonium chloride to the mixture before use.

Marckwald¹ first recognized that phototropism was a new phenomenon and considered it a truly reversible photo-reaction. Among the first organic compounds reported which exhibited phototropy were benzo[c][1,8]naphthyridine (listed as anhydrous quinoquinoline hydrochloride) and tetrachloro-1(2)-ketonaphthalenone which were prepared by Marckwald. In the same year Biltz¹²⁻¹⁴ observed the photo-

tropy of benzalphenylhydrazone and certain osazones. However, Wislicenus¹⁵ had noticed the reversibility of colour of benzalphenylhydrazone as early as 1893.

Both inorganic and organic compounds exhibit phototropy but most phototropic substances are organic in nature. Several hundred compounds are known to be phototropic in the solid state. In addition, a number of compounds exhibit phototropism in solution; most of these do not show the property in the solid state.

In scientific literature there is a distinction between phototropic, phosphorescent and fluorescent substances. The last two absorb light and then begin to reemit it. A few phosphorescent substances change colour when exposed to light but revert to their original colour in the dark. When a phosphorescent substance which changes colour on exposure to light is brought from the dark into the light, the colour of the substance changes until an equilibrium is reached between the rates of absorption and emission of light. The changes which occur in substances as they exhibit the phototropic phenomenon are different from the changes that occur in fluorescence and phosphorescence for there is no observable emission of radiation after the exciting radiation is removed as is found in fluorescent and phosphorescent processes.

There are very few quantitative data on the rate at which phototropic solid substances undergo their colour changes. Generally it can be said that the time required for bright sunlight to produce a pronounced change in colour is of the order of a few seconds to many minutes. The reverse change in the dark requires from a minute to several weeks. Solutions generally show a colour change on exposure to light of the order of a microsecond to a few seconds while the reverse change requires from a few seconds to several days.

A wide variety of substances shows phototropism and a variety of different explanations has been given to interpret the phenomenon. These explanations have been summarized in Section 5. In earlier sections of this review the compounds which show photochromism have been listed and experimental observations of the phototropic phenomenon have been described.

2 LISTING OF PHOTOTROPIC SOLIDS AND SOLUTIONS

Most of the earlier work on phototropy was done with solids while a large portion of the more recent work deals with the phototropy of solutions. In this section an effort has been made to list the phototropic materials that have been reported in the literature, both solids and solutions. No effort has been made

pism, the letter n indicates absence of phototropy while the letter r indicates reverse phototropy. The superior number indicates the reference from which the information about the compound was obtained.

2.1 Solid organic materials

2.1.1 Anils or Schiff bases

The condensation products of aldehydes and primary amines are called anils or Schiff bases.

Table 1 ANILS

Amine	Aldehyde						
	Salicylaldehyde	5-Bromosalicylaldehyde ¹⁰	3,5-Dibromosalicylaldehyde ¹⁷	4-Hydroxybenzaldehyde ¹⁵	2-Hydroxy-3-methoxybenzaldehyde ¹⁰	<i>o</i> -Nitrobenzaldehyde ²⁰	6-Nitroveratraldehyde ²⁰
<i>m</i> -Aminobenzoic acid	p ⁹	n	—	n	—	—	—
<i>p</i> -Aminobenzoic acid	p ²¹	—	—	n	—	—	—
<i>p</i> -Aminobiphenyl	—	—	—	—	—	p	—
<i>o</i> -Aminocinnamic acid	p ²⁰	—	—	—	—	—	—
<i>p</i> -Aminoethylbenzoate	p ²²	—	—	—	—	—	—
Aniline	p ¹⁰	n	n	n	n	—	—
<i>o</i> -Anisidine	p ¹⁰	n	—	p	n	p	—
<i>p</i> -Anisidine	p ¹⁰	n	—	n	n	—	p
<i>m</i> -Bromoaniline	p ¹⁰	—	—	n	n	—	—
<i>o</i> -Bromoaniline	p ¹⁰	n	—	n	n	—	—
<i>p</i> -Bromoaniline	p ¹⁰	p	n	p	n	—	—
<i>m</i> -Chloroaniline	n ²¹	n	—	n	n	—	—
<i>o</i> -Chloroaniline	p ²¹	n	—	n	n	—	—
α -Naphthylamine	n ²¹	p	n	n	—	p	—
β -Naphthylamine	p ²¹	n	n	n	n	p	—
<i>m</i> -Nitroaniline	—	—	—	—	—	p	—
<i>o</i> -Nitroaniline	—	—	—	—	—	p	—
<i>p</i> -Nitroaniline	—	—	—	—	—	p	—
<i>p</i> -Phenetidine	—	—	—	—	—	p	—
<i>m</i> -Phenylenediamine	p ²¹	—	n	—	—	—	—
<i>m</i> -Toluidine	p ²³	n	—	n	n	—	—
<i>p</i> -Toluidine	p ¹⁶	n	n	n	n	—	—
1,2,4-Xylidine	n ²³	n	—	p ²⁴	n	—	—
1,2,5-Xylidine	n ²³	n	—	n ¹⁰	n	—	—
1,3,4-Xylidine	p ²¹	—	—	n	n	—	—

Key p = phototropic; n = non-phototropic

to list all of the compounds which have been tested and found to be non-phototropic. However, in certain tables where convenient, some non-phototropic compounds are cited.

In the tables which follow the letter p indicates that the substance shows phototro-

Several hundred anils have been examined for phototropy, but only a few have been found to possess the property. Those showing phototropy are summarized in Table 1. A blank space indicates that the anil has not been examined for phototropic character. The

phototropic anils are colourless or light yellow in the dark and generally red in sunlight.

de Gaouck and Le Fevre²⁵ made an interesting analysis of the anils. They concluded that of the 300 anils known at the time of their publication only 25 had been reported to show phototropism and of these, 18 were derivatives of *o*-hydroxybenzaldehyde and 3 were derivatives of *p*-hydroxybenzaldehyde. They reported that in compounds of the type $2,5\text{-X(OH)C}_6\text{H}_3\text{-CH=NC}_6\text{H}_2\text{Y}_3$ if X is any group other than H, phototropism does not occur; the influence of Y upon the phototropic process is very marked, for although salicylidene-*m*-toluidine, salicylidene-aniline and salicylidene-*p*-bromoaniline show phototropism, salicylidene *o*- and *p*-toluidines and *p*-chloroaniline do not exhibit the phenomenon. These authors concluded that the phototropic mechanism must consist of a material interaction of molecules in the lattice and not in some rearrangement undergone by the molecules.

2.1.2 Disulphoxides

Bis(*p*-acetamidophenyl)disulphoxide is phototropic when mixed with about 0.1% of bis(*p*-acetamidophenyl)disulphide^{26,27}. Pure bis(*p*-acetamidophenyl)disulphoxide is not phototropic. The disulphide must be in solid solution since mechanical mixing of the two components does not produce phototropy; also, the disulphide must be present in the proper amount for the disulphoxide to show phototropism. Other phenyl disulphides containing amino groups, or substituted amino groups, *para* to the sulphur atoms may replace the acetamidodisulphide. However, *meta* and *ortho* compounds are not phototropic. Other disulphur compounds²⁷ that are phototropic are bis(4-acetamido-1-naphthyl)disulphoxide, bis(4-acetamido-*m*-tolyl)disulphoxide, and *p*-acetamido-phenyl ester of *p*-chlorothiobenzenesulphonic acid. The phototropy of these sulfoxides may be due to traces of a disulphide but this has not been proved.

2.1.3 Hydrazones

The phototropic hydrazones are listed in Table 2. The data in the table refer to the hydrazone formed by the condensation of the hydrazine named over the datum, and the aldehyde, ester or α -diketone named on the side. In listing

the hydrazine, only the distinctive part of the name of the hydrazine is given. For example, "phenyl" represents phenylhydrazine, etc.

2.1.4 Osazones

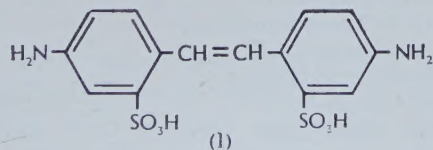
The phototropic osazones are listed in Table 3. With the exception of the phenylosazones of benzil, anisil and piperil, it appears that only one modification of the osazones has been studied for phototropy. The phenylosazones just cited show phototropy in both modifications. In those cases where only one stereoisomer has been studied the letter β is used to designate the modification.

2.1.5 Semicarbazones

Some of the semicarbazones possess very interesting phototropic properties. Cinnamaldehyde semicarbazone is white when freshly prepared and its colour does not change if it is stored in the dark or in the light. However, after exposure to sunlight for an hour and then storage in the dark the compound becomes yellow; exposure of the yellow form to light brings back the colourless form. The process can be repeated again and again⁴⁵. Recrystallization of either the yellow or white form always yields the white modification. The semicarbazones of *o*-methoxycinnamaldehyde, *m*-methoxycinnamaldehyde and *p*-methoxycinnamaldehyde as well as the phenyl semicarbazones of *o*-methoxycinnamaldehyde and *p*-methoxycinnamaldehyde all exhibit this peculiar behaviour to light⁴⁶. The phototropic semicarbazones are listed in Table 4.

2.1.6 Stilbene derivatives

Stobbe and Mallison⁵³ found that certain derivatives of 4,4'-diamino-2,2'-stilbenedisulphonic acid (1) are phototropic. The colour



changes of all of these derivatives are from colourless or yellow in the dark to pink in the light and are reversible. The known phototropic derivatives are 4,4'-diformamido-2,2'-stilbenedisulphonic acid, 4,4'-bis(*p*-formamidobenzamido)-2,2'-stilbenedisulphonic acid, 4,4'-diacetamido-2,2'-stilbenedisulphonic acid and

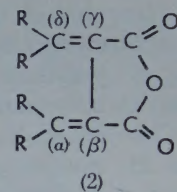
many of its salts, 4,4'-bis(4-acetamidobenzoylenamido)-2,2'-stilbenedisulphonic acid and 4,4'-bis[*p*-(*p*-acetamidobenzamido)benzamido]-2,2'-stilbenedisulphonic acid.

2.1.7 Succinic anhydrides

Stobbe^{3,38,54} and later Hanel⁵⁵ studied a whole series of succinic anhydrides ("fulgides") (2) and their derivatives. Since the four R-groups may be substituted by a variety of organic radicals, and as the resulting compounds may exhibit *cis-trans* isomerism, the number of derivatives of these parent substances is very large. Stobbe found that some of the sodium

salts of the succinic acids may or may not show phototropy depending on whether or not the salt is anhydrous or contains water of crystallization.

Most of the substituted succinic anhydrides



are yellow to red in the dark and prolonged exposure to light darkens the sample. The

Table 2 HYDRAZONES

Hydrazine										
Aldehyde, Ester, Ketone and α-Diketone	Anisyl ²⁸	<i>p</i> -Bromophenyl ²⁹	<i>m</i> -Chlorophenyl ³⁰	<i>p</i> -Chlorophenyl ³⁰	β-Naphthyl	Phenyl	<i>m</i> -Tolyl ³¹	<i>p</i> -Tolyl ³²	1,3,4-Xylyl ³³	1,3,5-Xylyl ³⁴
<i>o</i> -Aminobenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
Anisaldehyde	n	n	p	n	n ³²	p ³⁵	n	n	p	n
Benzaldehyde	p	p	n	p	p ³⁵	p ¹²	p	p	p	—
5-Bromosalicylaldehyde	—	—	—	—	—	p ¹⁶	—	—	—	—
Cinnamaldehyde	p	p	p	p	p ³²	p ³¹	p	p	n	p
Cuminaldehyde	p	p	p	p	p ³²	—	p	p	p	—
<i>p</i> - <i>n</i> -Decyloxybenzaldehyde	—	—	—	—	—	p ³⁷	—	—	—	—
Diethyl dimethyloxalacetate	—	—	—	—	—	p ³⁸	—	—	—	—
2,4-Dihydroxybenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
<i>p</i> -Dimethylaminobenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
2-Furaldehyde	—	—	—	—	p ³⁰	n ³⁶	—	p ³⁶	—	—
<i>m</i> -Hydroxybenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
<i>p</i> -Hydroxybenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
9-Ketofluorene-4-carbonic (acid ester)	—	—	—	—	—	p ³	—	—	—	—
<i>m</i> -Methoxybenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
<i>o</i> -Methoxybenzaldehyde	—	—	—	—	p ³	—	—	—	—	—
5-Methyl-1-(3,4-methylenedioxy- phenyl)-1-hexen-3-one	—	—	—	—	—	p ³⁰	—	—	—	—
<i>p</i> - <i>n</i> -Nonoxybenzaldehyde	—	—	—	—	—	p ³⁷	—	—	—	—
1-Phenyl-1-hexen-3-one	—	—	—	—	—	p ^{30, 40}	—	—	—	—
1-Phenyl-1-penten-3-one	—	—	—	—	—	p ^{30, 40}	—	—	—	—
Piperonal	p	n	p	n	p ³	n ³¹	p	p	p	n
Salicylaldehyde	n	p	—	n	n ³³	—	—	—	p	—
<i>m</i> -Tolualdehyde	—	—	—	—	p ³	—	—	—	—	—
<i>o</i> -Tolualdehyde	—	—	—	—	p ³	—	—	—	—	—
<i>p</i> -Tolualdehyde	p	n	p	p	p ³³	p ³¹	n	n	p	n
Vanillin	n	n	—	n	p ³³	—	—	n	n	—
Veratraldehyde	—	—	—	—	p ³	—	—	—	—	—

Key p = phototropic; n = non-phototropic

succinic acids and their derivatives are white, or in a few cases a light yellow, and change to yellow or to red on exposure to light. Stobbe did not study the effect of ultraviolet light on these compounds and points out that some of the compounds he lists as non-phototropic might be phototropic in ultraviolet light.

2.1.8 Other solid organic compounds

In addition to the classes of phototropic compounds listed in the preceding sections there are some other widely different organic compounds that show phototropy. These compounds are anhydrous benzo[c][1,8]naphthyridine¹, N-(5-bromosalicylidene)benzylamine⁵⁶, N-(5-bromosalicylidene)methylamine⁵⁶, salicylidene-*p*-anisidine⁵⁷, 2-hydroxy-3-methoxybenzylidene-*p*-xylidene⁵⁷, tetrachloro-1(2 or 4)-naphthalenone^{1,58,59,60}, spirans^{61,62}, *o*-nitrobenzylidene isonicotinic acid hydrazide⁶³, 2,3-epoxy-2-ethyl-3-phenyl-1-indanone⁶⁴, *p*-diethyl- and *p*-dimethyl-aminophenylimino-camphor⁶⁵, brucine salts of bromo- and chloronitromethionic acid⁶⁶, diphenacyldiphenylmethane^{67,68}, 2,4,4,6-tetraphenyl-1,4-dihydropyridine^{67,68}, 2,4,4,6-tetraphenyl-3,5-dibenzoyltet-

solution. No careful study has been made of the role of the solvent but some workers have suggested that the intensity of the colour is dependent upon the solvent. Some examples are 3-(1-naphthylamino)camphor⁷⁸⁻⁸¹, 3-(*m*-aminoanilino)camphor^{78,79,81}, 3-(5,6,7,8-tetrahydro-1-naphthylamino)camphor^{78,79,81}, chlorophyll^{82,83}, and a large number of dyes^{25,77,82,84-95,102-105}. Several dehydrobianthrone^{94,97-99}, some aromatic-substituted chloromethanes⁹⁶, and 2- and 4-(2',4'-dinitrobenzyl)pyridine^{100,101} also exhibit phototropism in solution.

2.3 Solid inorganic compounds

The number of inorganic compounds exhibiting phototropy is considerably less than the number of organic compounds.

2.3.1 Alkaline earth sulphides and titanates
Mourelle carried out a number of studies on the phototropy of alkaline earth sulphides¹⁰⁶⁻¹¹⁷ and concluded that there must be traces of an active ingredient present such as manganese or bismuth before they would exhibit phototropy.

Barium, calcium and strontium titanates with small amounts of Fe(II), Zn(II), Sb(V)

Table 3 OSAZONES

Aldehyde	Hydrazine									
	Diphenyl ¹¹	Methylphenyl ¹¹	α -Naphthyl ¹²	β -Naphthyl		Phenyl ^{12a}	<i>m</i> -Tolyl ^{12a}	<i>o</i> -Tolyl	<i>p</i> -Tolyl	1,3,4-Xylyl ¹²
Anisil	n	n	p	p(β) ³⁸		p	p(β)	n(β) ⁴³	p(β) ⁴³	p
Benzil	—	—	n	p(β) ⁴⁴		p	p(β)	p(β) ⁴⁴	p(β) ⁴⁴	p
Cuminil	—	—	—	—	p(β)	—	—	—	—	n
Piperil ...	—	n	p	p ⁴⁴	p	p	p ⁴⁴	p(β) ⁴⁴	p(β) ⁴⁴	p

Key p = phototropic; n = non-phototropic

rahydropyran^{67,68}, yellow modification of α -azoxynaphthalene⁶⁹, the condensation products of 1,2-diphenyl-3,5-diketopyrazolidine with ϕNO_2 , $\text{ONC}_6\text{H}_4\text{OH}$ and $\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2$, tetrabenzoylethylene⁷¹, *o*-nitrobenzylidenedesoxybenzoin⁷², *p*-nitrobenzylidenedesoxybenzoin⁷², N-(3-pyridyl)syndone^{73,74}, 2-(2',4'-dinitrobenzyl)pyridine^{75,76}, and derivatives of 4-aminobenzene⁷⁷.

2.2 Solutions of organic compounds

A number of compounds show phototropy in

and V(V), show phototropy¹¹⁸, and it was concluded that for an impurity to be effective it must have an ionic radius near that of Ti^{4+} , and a different valence to make electron transfer possible. Calcium titanate¹¹⁹ was reported as exhibiting phototropy in the presence of both oxygen and moisture.

2.3.2 Mercury compounds

Data from Rao and Watson¹²⁰ on phototropic mercury compounds are given in Table 5. The following mercury compounds have also

been described: I-Hg-S-S-Hg-I¹²⁷, HgBrCl, HgICl, HgIBr²²; and HgI·2HgS¹²⁸. A mixture of mercury (I) and silver iodides produced by toning photographic images of silver with mercury (II) iodide is phototropic¹²⁹, as are certain mixtures of Ag₂S and HgI₂¹³⁰.

2.3.3 Titanium compounds

The phototropic nature of rutile was first ob-

The phototropic effects with anatase, rutile, anatase-rutile mixtures, and TiO₂ contaminated with Ni, Cr, Cu, Sm, Pr, Yb and Nd compounds have been systematically investigated¹³⁶.

2.3.4 Oxides

Many oxides, such as Nb₂O₅, Al₂O₃, SnO₂ and ZnO become phototropic when contaminated

Table 4 SEMICABAZONES

Aldehyde and Ketone	Semicarbazone	Thiosemicarbazone	Phenylsemicarbazone
Cinnamaldehyde	r ⁴⁷	p ⁴⁶	—
1-(2-Hydroxyphenyl)-1-penten-3-one	—	—	p(α) ⁵¹
4-(4-Hydroxyphenyl)-3-buten-2-one	—	p ⁵¹	p(α) ⁵¹
1-(4-Isopropylphenyl)-1-hexen-3-one	—	p ⁵¹	p(α) ⁵¹
1-(4-Isopropylphenyl)-1-penten-3-one	—	p ⁵¹	p(α) ⁵¹
4-Methyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one	—	p ⁵¹	p(α) ⁵¹
5-Methyl-1-(3,4-methylenedioxyphenyl)-1-hexen-3-one	p ³⁹	—	p(α) ³⁹
5-Methyl-1-(1-naphthyl)-1-hexen-3-one	p ^{40, 48}	—	—
1-(3,4-Methylenedioxyphenyl)-1-penten-3-one	—	p ⁵¹	p(α) ⁵¹
<i>m</i> -Methoxycinnamaldehyde	r ¹⁵	—	n ⁴⁶
<i>o</i> -Methoxycinnamaldehyde	r ⁴⁶	p ⁴⁶	r ⁴⁶
<i>p</i> -Methoxycinnamaldehyde	p ⁴⁶	n ⁴⁶	—
1-(2-Methoxyphenyl)-4-methyl-1-penten-3-one	—	p ⁵¹	—
1-(4-Methoxyphenyl)-5-methyl-1-hexen-3-one	p ⁴⁶	—	—
1-(4-Methoxyphenyl)-1-penten-3-one	p ⁴⁶	—	—
4-(2-Methoxyphenyl)-3-methyl-3-buten-2-one	—	p ⁵¹	—
4-(4-Methoxyphenyl)-3-ethyl-3-buten-2-one	—	p ⁵¹	p(α) ⁵²
5-(4-Methoxyphenyl)-2-penten-3-one	p ⁵⁰	—	—
6-(4-Methoxyphenyl)-2-methyl-5-hexen-4-one	p ⁵⁰	—	—
1-(1-Naphthyl)-1-hexen-3-one	p ^{40, 48}	—	—
2-Nitrochalcone	p ⁴⁰	—	—
3-Nitrochalcone	p ⁴⁰	—	—
1-Phenyl-1-hepten-3-one	p ⁴⁶	—	—
1-Phenyl-1-penten-3-one	p ⁴⁶	—	—
4-Phenyl-3-buten-2-one	—	p ⁵¹	p(α) ⁵¹
5-Phenyl-4-penten-3-one	p ⁵⁰	—	—

Key p = phototropy; r = reverse phototropy; n = non-phototropy

served by Lee¹³¹ and by Parmalee and Badger¹³², Williamson^{47,133,134} and Weyl and Forland¹³⁵ reported that some varieties of commercial TiO₂ and TiO₂ contaminated with iron (added as Fe₂O₃) showed reversible darkening in daylight while pure TiO₂ gave no perceptible darkening. A concentration of 0.2% Fe₂O₃ gave maximum photochromism.

by impurities found effective for TiO₂^{136,137}.

2.3.5 Zinc sulphide

The phototropic properties of lithopone have been the subject of a number of investigations and speculations^{8,10,11,52,138-147}. Certain research workers have shown that the phototropic properties of lithopone are due to zinc sulphide^{11,138,140,143}.

2.3.6 Miscellaneous compounds

Copper(I) chloride, copper (I) bromide^{148,149}, bismuth oxalate¹⁵⁰, lithium imide¹⁵¹, pink hackmanite¹⁵¹, and sodalite¹⁵² all show phototropy. The phototropy of copper (I) halides is temperature sensitive and above 75° C practically no spectral sensitivity is observed.

2.4 Solutions of inorganic compounds

A solution of molybdenum trioxide in selenium oxychloride is normally light yellow but becomes indigo blue in sunlight and reverts to

light absorbed by a substance are active in producing a phototropic change; that is the phototropic process follows the Grotthuss-Draper Law which states that only those wavelengths which are absorbed by a reacting system are effective in inducing a chemical change. The time required for a phototropic substance in solution to undergo an appreciable colour change when exposed to light varies with the solution and the conditions of illumination; however, it seldom takes more than two minutes in bright sunlight for the change

Table 5 PHOTOTROPIC DATA ON MERCURY COMPOUNDS¹²⁰

Substance	Colour before exposure	Darkening time (min.)	Time for recovery (day)
Hg(Cl)CNO	Pale brown	30	2
Hg(Br)CNO	Pale yellow	15	2
Hg(I)CNO	Golden yellow	3	1.5
Hg(Cl)CNS (Also ref. 22)	White	20	2
Hg(Br)CNS (Also ref. 22)	White	2	2
Hg(I)CNS (Also ref. 22, 121, 122)	Orange yellow	1	1.5
Hg(Cl)CNSe	Pale yellow	20	1.5
Hg(Br)CNSe	Yellow	2	1
Hg(I)CNSe	Orange	<2	1.5
Hg(HS)CNS (Also ref. 122, 123)	Lemon yellow	<1	2
Hg(HS)CNSe	Pale brown	90	3
HgCl ₂ ·2HgS (Also ref. 121)	White	10	2
HgBr ₂ ·2HgS (Also ref. 121, 124, 125)	Pale yellow	3	2
HgI ₂ ·2HgS (Also ref. 121, 124-126)	Orange yellow	<1	2
HgCl ₂ ·2HgSe	White	120	2
HgBr ₂ ·2HgSe	Pale yellow	45	1.5
HgI ₂ ·2HgSe	Pale brown	5	1.5
Hg(SCN) ₂ ·2HgO	Yellow	200	3
Hg(SCN) ₂ ·2HgS	Yellow green	3	2
Hg(CNSe) ₂ ·2HgS	Brown	6	1.5

the original colour in the dark¹⁵³. An aqueous solution of potassium ferrocyanide which contains a little phenolphthalein is yellow in the dark but turns red in light¹⁵⁴. The stable colour returns when the solution is placed in the dark. A solution of 7 ml. of 1 per cent L(+)-ascorbic acid, 1.5 ml. of 45% acetic acid and 25 ml. of 1% copper acetate forms a phototropic system, which changes from yellow to brown-black on exposure to light¹⁵⁵.

3 PROPERTIES OF SOLUTIONS EXHIBITING PHOTOTROPY

3.1 Exciting radiation

A number of workers^{80,95} (also refs. 59, 156) have reported that only those wavelengths of

to take place and in some cases the change is of the order of a microsecond.

Further work on phototropic solutions is still needed to develop quantitative relationships between the wavelength of the light used and the colour change, between the intensity of radiation and the speed of the colour change, and between the intensity of the light and the time of exposure to bring about maximum colour change. Some recent work has shown that the exciting radiation for the phototropic process in solutions is in the ultraviolet region or in the lower range of the visible spectrum, but no general conclusion of a quantitative nature can be drawn concerning the relationship between the exciting radiation and phototropy.

3.2 Conductivity

Studies on the conductivity of solutions exhibiting phototropy are rare and those studies which are available are contradictory. Lifschitz and Joffé⁸⁸, who measured the conductivity of certain triphenylmethane dyes in absolute ethanol before and after irradiation, divided the dyes into two categories, according as the conductivity did or did not return to the original value. Malachite green leucocyanide and brilliant green leucocyanide were in the first category; crystal violet leucocyanide, pararosaniline leucocyanide and auramine were in the second. They also reported that the alcoholic solution of victoria blue leucocyanide, which becomes coloured in the light but does not fade in the dark, shows a specific conductance that steadily increases when exposed to light and does not fall off when placed in the dark.

The most reliable work on conductivity was done by de Gaouck and Le Fevre who prepared solutions of malachite green leucocyanide and brilliant green leucocyanide and re-examined the conductivity of the alcohol solutions. These authors confirmed the increase in conductivity which accompanies illumination and colour development. However, the solutions did not regain their original conductivity after the excited solution had stood in the dark. This was attributed to the fact that the alcohol contained a small amount of water which resulted in the formation of hydrogen cyanide by hydrolytic action. Benzene solutions of the dyes did not undergo any visible alteration under daylight or light from a mercury discharge tube. Figure 1 illustrates the type of conductivity data obtained by de Gaouck and Le Fevre²⁵.

3.3 Fatigue

Very little data are available on the stability of phototropic solutions. Some systems will certainly deteriorate with time because of side reactions, reactions with the solvent, etc., while others should be phototropic indefinitely. An

colour change after long exposure to light^{84,85}. Solutions of (1-naphthylamino)camphor and 3-(*m*-aminoanilino)camphor⁷⁸ in chloroform both lose their power to undergo the phototropic change with repeated exposures. Gould and Brode¹⁵⁷ claimed that monoazo dyes such as 4-dimethylaminoazobenzene dissolved in benzene did not show phototropic decay, but they did not carry out a large number of exposures on any one solution.

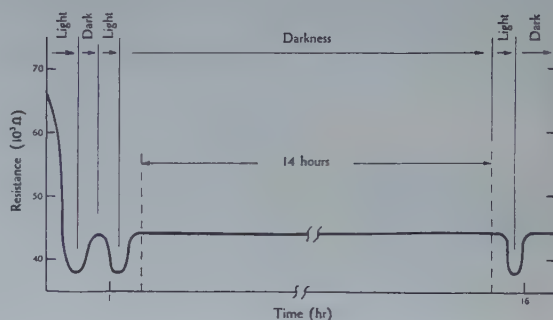


Figure 1 Resistance of a solution of malachite green leucocyanide as a function of time (after de Gaouck and Le Fevre²⁵)

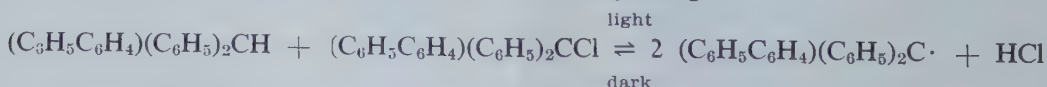
3.4 Optical rotation

It has been reported⁷⁹ that a solution containing 0.726 g of (1-naphthylamino)camphor in 100 ml. of chloroform showed a specific rotation of 126° using the green line of mercury ($\lambda = 5461\text{\AA}$). After exposure to sunlight for six minutes, the specific rotation was 186.6°. The abstract to the article does not give information as to whether the reverse change was complete but only mentions that the reverse change in the dark required several days.

3.5 Mechanism of colour changes

A few investigators have attempted to interpret the cause of phototropy in solutions.

Schlenk and Herzenstein⁹⁶ suggested that triphenylmethane derivatives in solution, which change their colour in light, undergo the following change:



etheral solution of bis(10-hydroxyphenanthryl)-9-amine loses its capacity to undergo

They substantiate their view by pointing out that diphenylbiphenylmethyl and phenyldi-

biphenylmethyl in benzene solution are relatively sensitive to hydrogen chloride, but stable to sunlight.

Lifschitz and co-workers^{87,88,90,158} proposed the mechanism shown in Fig. 2 for the photolysis and dark reaction of malachite green leucocyanide in absolute alcohol. However,

Einstein equivalence law held with an accuracy of 2.5% in absolute value for the photolysis of malachite green leucocyanide in ethanol. Germann and Gibson¹⁶¹ concluded that the malachite green leucocyanide in ethanol containing a little water does not regenerate the leucocyanide or the leucocarinol as the end

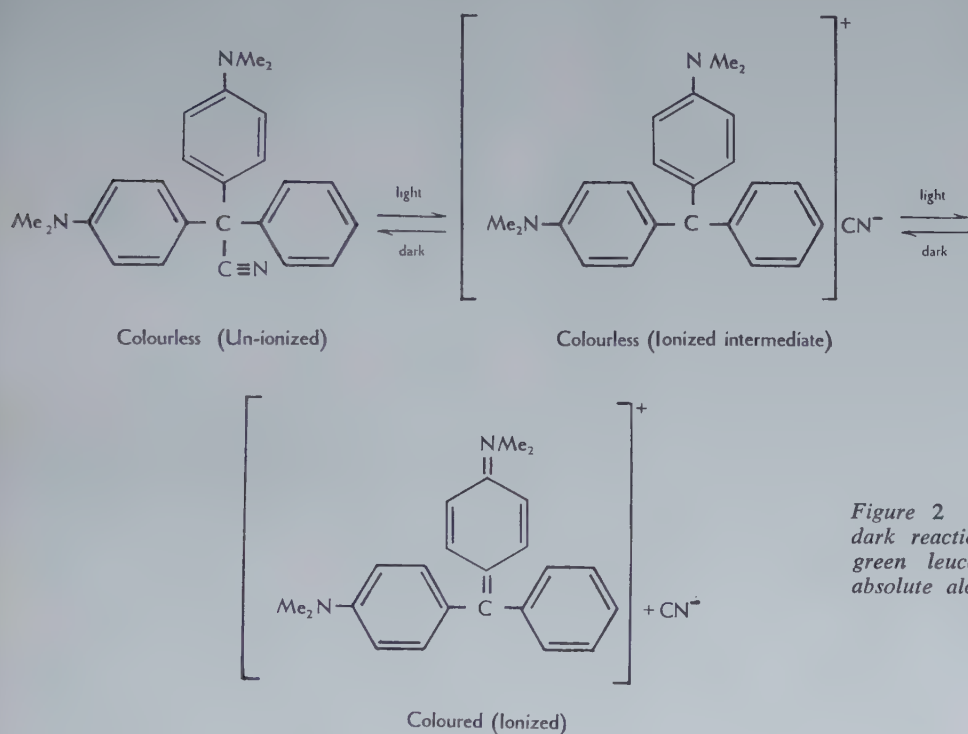


Figure 2 Photolysis and dark reaction of malachite green leucocyanide in absolute alcohol

Harris, Kaminsky and Simard¹⁵⁹ favour the mechanism shown in Fig. 3 for the photolysis of malachite green leucocyanide and for the dark reaction. The final product then of the

product. They did not identify the final product but only defined it as a colourless, light-sensitive substance which absorbed in the neighbourhood of 350 $m\mu$.

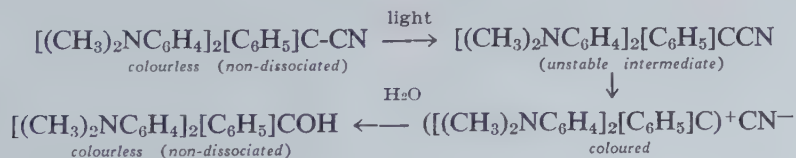


Figure 3 Photolysis of malachite green leucocyanide proposed by Harris et al.¹⁵⁹

dark reaction is the colourless carbinol and not the original leucocyanide. The unstable intermediate is proposed but the authors found no evidence for it.

Harris and Kaminsky¹⁶⁰ found that the

Calvert and Rechen¹⁶² confirmed the malachite green leucocyanide photolysis results of Harris, Kaminsky and Simard¹⁵⁹ and found a quantum yield of 1.02 for malachite green leucocyanide in absolute ethanol at a wave-

length of 313 m μ . Weyde and Frankenburger^{163,164} found that ethanol solutions of crystal violet leucocyanide and crystal violet sulphite could be used to measure small intensities of ultraviolet radiation. The leucocyanide has a quantum efficiency of one; the sulphite solution is more stable with time and thus can be used for many different exposures.

Singh⁷⁸ proposed that the phototropic character of 3-(1-naphthylamino)camphor in chloroform might be due to a keto-enol equilibrium. In a later paper, Singh and Bhaduri⁸⁰

and photochemical changes. A similar mechanism has been proposed by Lifschitz and Joffé⁸⁷ to explain the mechanism of the colour change of phototropic triphenylmethane dyes.

A study of the photochemical properties of thionine-iron(II) systems in water was made by Rabinowitch^{165,166} who proposed the equilibrium shown in Fig. 5. At low concentrations of thionine, the extent of bleaching is proportional to the first power of the light intensity, and inversely proportional to the concentration of the iron (III) ion. Under

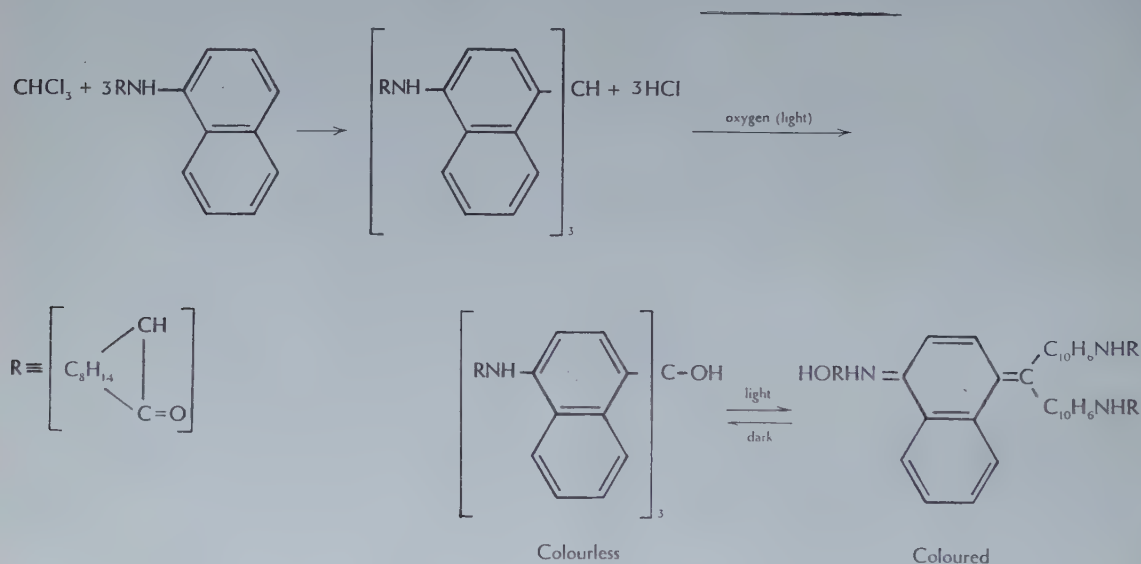


Figure 4. Mechanism of colour change of camphor derivatives proposed by Singh and Bhaduri⁸⁰

concluded that the mechanism of the colour change of camphor derivatives in solution was due to formation of a quinoid structure. The acidity of the solution after exposure to sunlight and the observation that only halogen containing solvents, which contain two or three atoms of halogen attached to the same carbon atom, can bring about the phototropic change may be explained in such a scheme. They proposed the mechanism shown in



Figure 5 Mechanism proposed by Rabinowitch^{165,166} for photochemical properties of thionine-iron (II)

Figure 4 which requires that the solvent takes part in the process. Singh and Bhaduri found that the stereoisomeric 3-(1-naphthylamino)-camphors (*d*, *l*, *dl*) exhibit identical phototropic

favourable conditions the system described above requires only a few seconds to reach both its stationary state in light and its stable state in the dark. The bleaching is completely reversible in the absence of oxygen but in the presence of oxygen, the reduced dye is partly reoxidized by oxygen and the effect is gradually weakened with continued exposure.

A carbon tetrachloride solution of tetra-

chloro-1-oxodihydronaphthalene at room temperature shows phototropy, remaining red for several minutes after exposure; longer exposure effects an irreversible secondary photo-

chemical reaction, manifested by a yellow colour that is attributed to dimerization to a quinol ether⁶⁰. Addition of chlorine to a colourless solution of tetrachloro-1-oxodihydronaphthalene prevents colouration upon exposure to light probably because the red form combines immediately with photochemically produced chlorine atoms.

Brode and Wyman^{167,168} interpreted the colour changes in the thioindigo dyes in benzene and in chloroform as due to a *cis-trans* equilibrium represented by one resonance modification (Fig. 6). In the case of the thio-

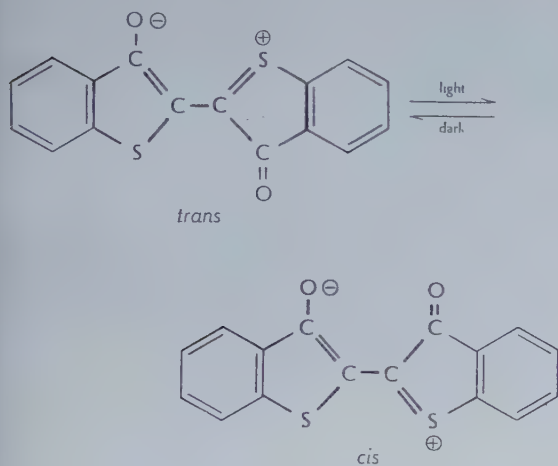


Figure 6 Colour changes in thio-indigo dyes according to Broda and Wyman^{167,168}

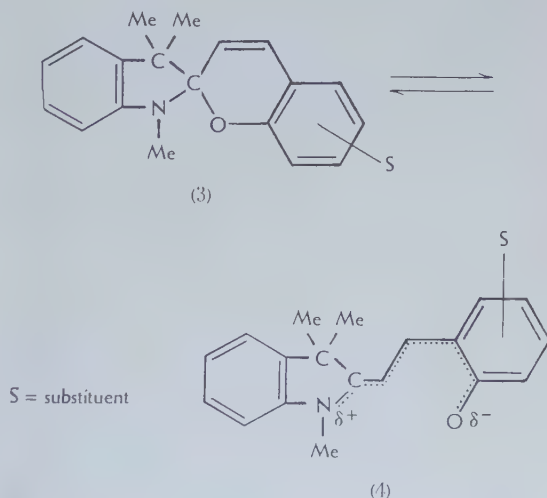
indigo dyes, the rate of return of the *cis*-form to the *trans*-form is so slow that it was possible to obtain a complete spectrum of solutions rich in the *cis*-isomer. On the other hand, monoazo dyes had a recovery time that was very rapid.

Likewise, Brode, Gould and Wyman¹⁶⁹ concluded that the phototropism of amine and hydroxyazo dyes was due to *cis-trans* isomerism. The irradiation of 4-amino and 4-hydroxyazo compounds caused partial isomerization to the unstable *cis*-form; subsequent standing in the dark results in a rapid reversal to the stable *trans*-form. Hydroxyazobenzenes show only partial conversion to the *cis*-form. This has been explained as due to stabilization of the *trans*-form by hydrogen bonding. For those systems that undergo a rapid deterioration Gould and Brode¹⁵⁷ have developed a rapid shutter illumination device to allow re-

liable measurements without decomposition.

Livingston and Ryan⁸⁸ attribute the phototropy of oxygen-free chlorophyll solutions in methanol to an excited metastable state of chlorophyll (perhaps the lowest triplet state) and to a radical. The radical is formed by the reaction of the metastable molecule with a molecule of the solvent. Under steady illumination only the radical and normal chlorophyll are present in detectable amounts. Both the radical and the metastable molecule are formed when the solution is illuminated with a flash of high intensity. These authors propose that the metastable molecules disappear by reaction with normal chlorophyll molecules (or probably by a simple first-order decay) while the radicals reform normal chlorophyll molecules by a second-order reaction. Abrahamson and Linschitz¹⁷⁰ extended the flash illumination studies of Livingston and Ryan and confirmed a far-red absorption band. Since extensive conversion under flash illumination occurs in both polar and non-polar solvents, it was concluded that at least one intermediate is formed by an intramolecular process rather than by a reaction in which the solvent participates. This transition may involve triplet state formation, internal rearrangement or both.

Chaudé and Rumf⁶¹ found that certain spirans in solution showed an equilibrium between the colourless form (3) and the coloured form (4). When exposed to ultraviolet radia-



tion the equilibrium shifts to the coloured form. Visible light causes a shift to the colourless form (3). Masse⁶² has studied form

(4) by the method of molecular orbitals and concluded that the energy differences are such that the shifts to the excited state (4) are expected. Berman, Fox and Thomson⁹² found that the thermal stability of state (4) can be increased by proper choice of substituent

10^{-6} sec^{-1} for the 6'-nitro-8'-fluoro derivative.

Holmes⁹¹ has studied the effect of the nature of the solvent and of the intensity of the radiation on the phototropic behaviour of malachite green leucocyanide. The solvents which he studied were ethanol, ethylene di-

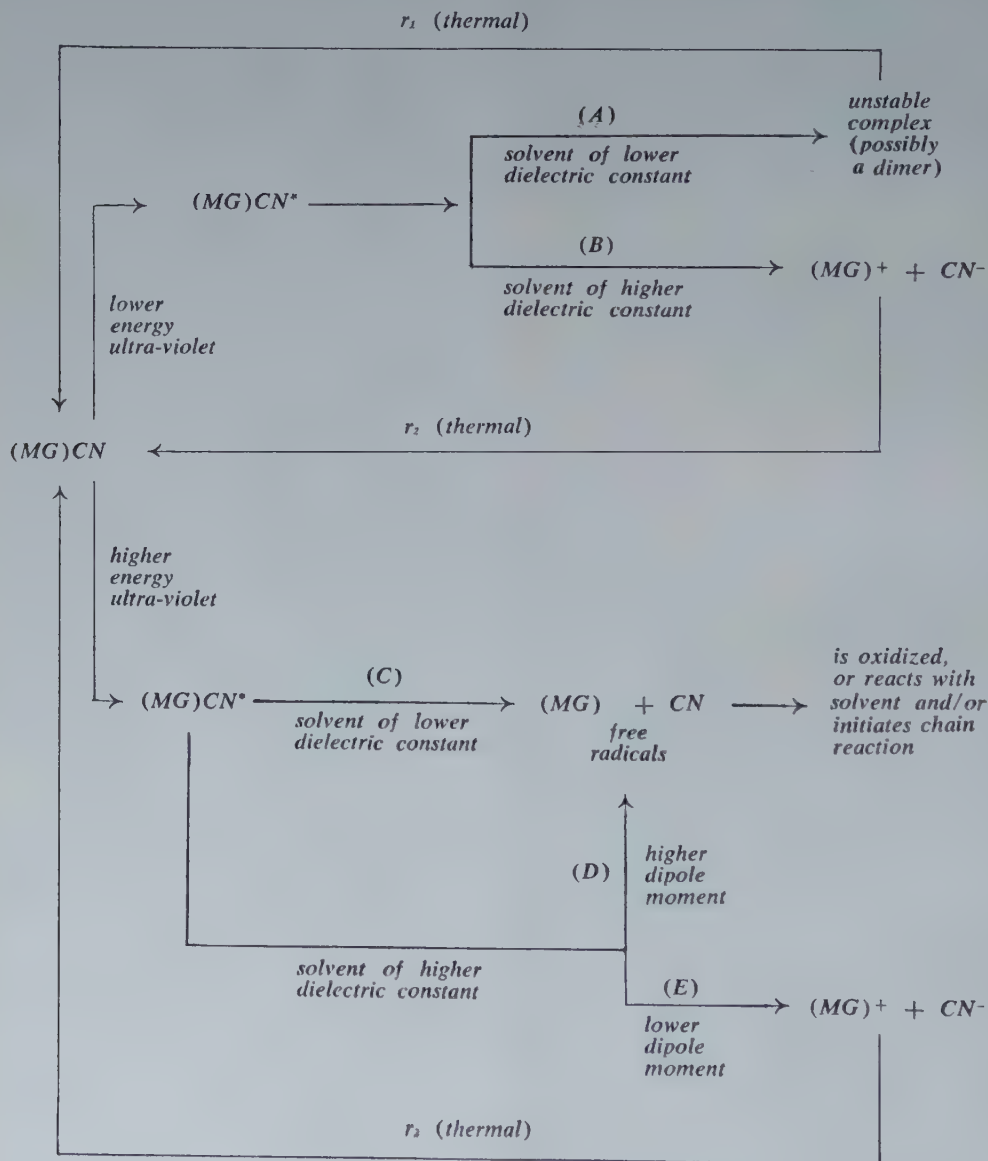


Figure 7 Mechanisms of phototropic behaviour of malachite green leucocyanide, $(MG)CN^*$ = activated molecule.

without apparent adverse effect on the photochemical process. For example the rate constant for ring closure $(4) \rightarrow (3)$ ranged from $1.3 \times 10^{-2} \text{ sec}^{-1}$ for 6'-methoxy-8'-nitro-1,3,3-trimethylindolinobenzopyrrolospiran to $6.3 \times$

chloride, ethylidene dichloride and cyclohexane as well as some mixtures of pairs of the last three. The results of Holmes' studies may be summarized as follows:

(1) The irradiation with ultraviolet light

will result in ionization of the leucocyanide in most cases. The dark reaction results in the formation of the leucocyanide. In a few cases the evidence supports an unstable complex (possibly a dimer).

(2) The larger the dipole moment of the solvent molecule the more capable it is of bringing about the ionization of the leucocyanide.

(3) The mechanisms of phototropic behaviour of malachite green leucocyanide as proposed by Holmes may be represented as in Figure 7.

(4) If cyclohexane is the solvent, mechanisms A and C predominate, while if ethylene dichloride is the solvent, mechanisms B, D and E predominate.

(5) With increase in the dielectric constant of the solvent there is a gradual shift from mechanisms A and C to B, D and E.

(6) Reverse reactions r_1 , r_2 are slow and the rates can be increased by heat.

Holmes concluded, from the mechanisms he proposed, that as the dielectric constant of the solvent increases the photoionization process

Hartley¹⁷¹ found that *trans*-azobenzene is converted into the *cis*-form on exposure of the solutions to light. Crystals of the *cis*-form can be kept indefinitely in the dark but are converted completely into the *trans*-form in solution. The conversion of *cis* to *trans* is a unimolecular reaction, not greatly dependent on the solvent, and the temperature coefficient corresponds to an energy of activation of 23 kcal mole⁻¹.

Kortüm and co-workers^{97,172} have studied the photochromism of dehydrodianthrone and its derivatives and found that they undergo a conversion into a green biradical when irradiated at low temperature (-78°C). This conversion is reversible on warming. From the fact that the conversion occurs in liquid solutions but not in solid solutions, it is concluded by these authors that the coloured species is a biradical; the coupling of the radicals occurs in such a manner that the planes of the radicals are at 90° angles to each other.

Spiropyrans show photochromism when dissolved in either ethanol-methanol (4:1 by

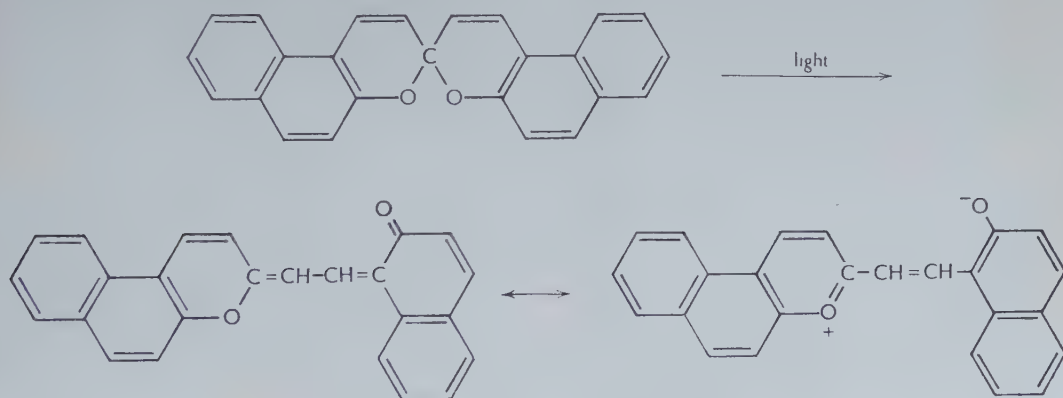


Figure 8 Phototropism of spiropyrans

requires less energy than the free radical process, the former predominating when lower energy quanta are absorbed by the solute.

Hardwick, Mosher, and co-workers^{100,101} have shown that both 2- and 4-(2',4'-dinitrobenzyl)pyridine in alcohol solutions exhibit photochromism. From ultraviolet and infrared spectra for the colourless and coloured forms they suggest that a hydrogen transfer may be taking place from the methylene group to the nitro group, intramolecularly, by means of a six-membered intermediate.

volume) or methylcyclohexane-isopentane (1:1 by volume)^{93,99}. The authors have proposed that the colour change may be due to various electronically excited metastable states. They also propose another tentative explanation that the spiropyran may "open up" when irradiated to give dyes that are geometrical isomers of the open merocyanine form. This mechanism will be represented using 3,3'-dimethylbisspiro-2,2'- β -naphthopyran as shown in Figure 8. The differences observed between the absorption curves of the postulated isomers were

found to be greater than those commonly encountered with geometric isomers and might be due to differences in the distance between the heteroatoms and to the contribution of the two main mesomers.

Neutral red (3-amino-6-dimethylamino-2-methylphenazine) has been found to exist in

creasing acidity (from pH 0 to 3.5). A green form NR^{3+} is formed from pH 3.5 to 9.5. All of these systems are phototropic and the colour changes are pH dependent.

The phototropic behaviour of 4-(*p*-dimethylaminobenzeneazo)phenylmercury (II) acetate has been explained as resulting from *cis-trans*

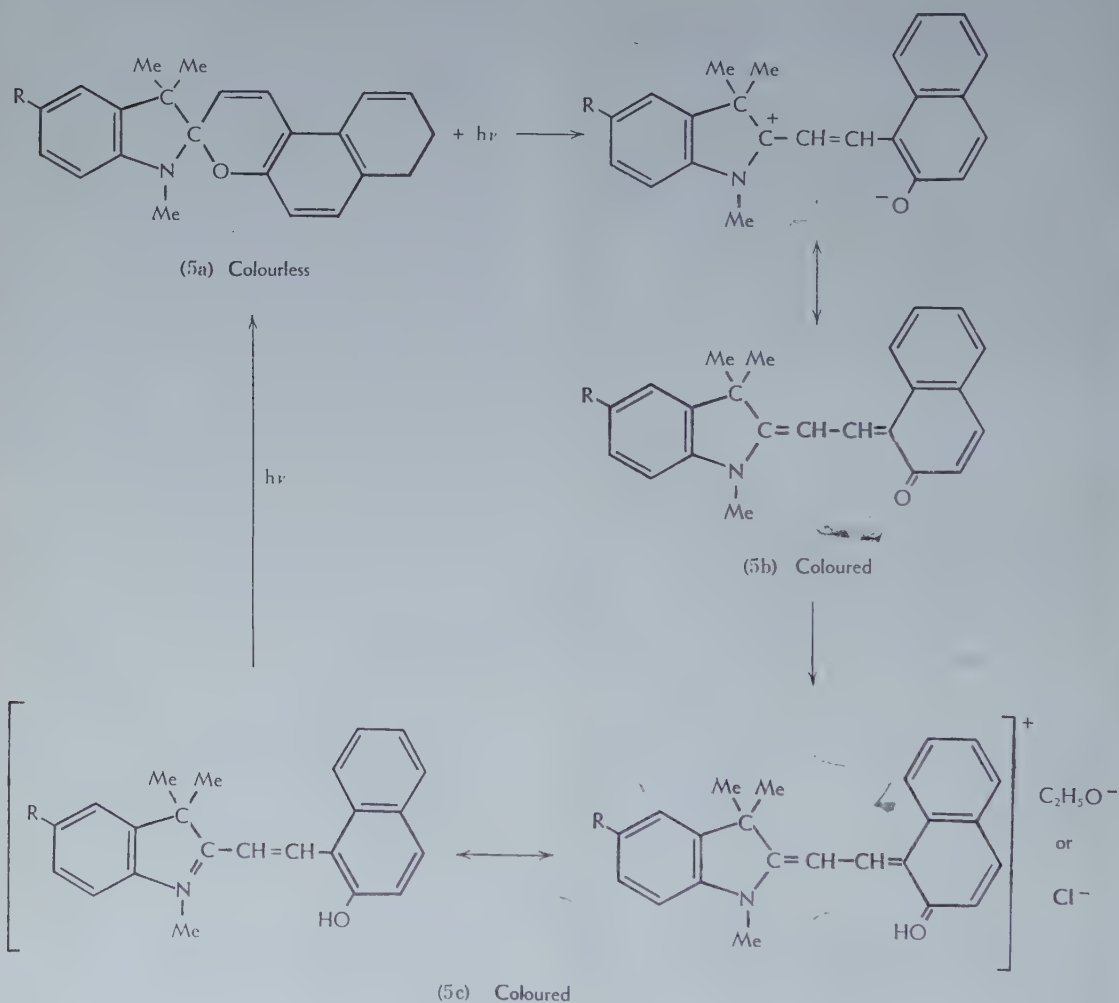


Figure 9 Photochromism of indolinospiropyran

six different forms¹⁰³. In the pH range of 7.5 to 13 it is yellow and the molecule is uncharged; at a pH of 5.5 to 7.5 as a carbonium boundary form; from pH of 0 to 5.5 the red NR^+ cation exists in solution and converts into the blue form NR^{2+} with in-

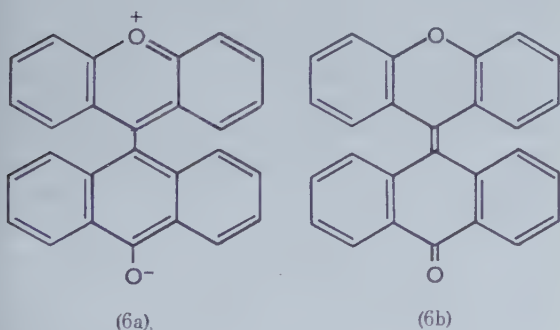
change⁸⁶. The transformation from *cis* to *trans* in dimethylformamide and in pyridine is first order and the rate constants have been established (see section 3.6 on kinetics).

Hirschberg⁹⁴ studied the photochromism of indolinospiropyran (5), 5-methoxyindolino-

spiropyran and N-methylacridinospiropyran and explained the phototropic cycle in these spiropyrans in a manner represented by the use of compound (5) as shown in Fig. 9.

In non-polar solvents (5b) is very stable. Excitation of this molecule by visible light is not enough to bring about the reclosure of the spiropyranic ring. Therefore, the reversion process from the coloured forms to the colourless ones by irradiation with visible light in non-polar solvents is very slow. 5-Methoxyindolinospiropyran, however, with the methoxy group can be easily reconverted on absorption of visible light into its colourless form. In polar solvents (e.g. ethanol) or in hydrochloric acid the coloured molecule (5b) is partially transformed into the quasi complex coloured salt (5c). 5-Methoxyindolinospiropyran and N-methylacridinospiropyran behave in a comparable fashion.

Lewis and Lipkin¹⁷³ proposed that photochromism of xanthylideneanthrone was due to steric isomerism in which the coloured form contains a higher contribution of the bipolar mesomer (6a), whereas in the colourless isomer the contribution of mesomer (6b) predominates. These forms may be represented as follows:



3.6 Kinetics and thermodynamics of the colour change

One of the first attempts to study the velocity of change of colour of a phototropic substance in solution was made on rosaniline sulphite solutions⁹⁵. The data show, in an approximate manner, a rapid change of intensity of colour with time for the first few minutes,

with a levelling off, followed by a gradual decrease in intensity after five or six minutes. Ariga¹⁷⁴ found that the velocity of the colour change of malachite green carbinol was directly proportional to the intensity of the light and practically independent of the temperature and the concentration of the alkali in the solution.

There is very little quantitative data on the rates of phototropic reactions. Livingston and Ryan⁸³ report that the metastable molecules of chlorophyll disappear to form radicals possibly by first-order decay while the radicals reform normal chlorophyll molecules by a second-order reaction. The half-life of both species (both the radical and metastable chlorophyll molecule are formed in comparable concentrations when the methanol solution is illuminated with a flash of high intensity) is about 5×10^{-4} sec at wavelengths of 468–477.5 m μ . Livingston, Porter and Windsor⁸² found the half-life values of the principal photo-chemical transient in chlorophylls and coproporphyrin in benzene or methanol to be between $2 \times$ and 5×10^{-4} sec. The original papers give details on the half-lives of the metastable molecules.

Table 6. Rate constants for thermal stability of ethanol solutions of some 1,3,3-trimethylindolino-benzopyrylospirans⁹².

Substituent	$k(\text{sec}^{-1})$
6'-nitro	4.28×10^{-5}
6'-nitro-8'-allyl	2.10×10^{-4}
6'-nitro-8'-fluoro	6.33×10^{-5}
6'-methoxy-8'-nitro	1.32×10^{-2}
5'-nitro-8'-methoxy	2.52×10^{-3}

Kinetics of the *cis* to *trans* change of 4-(*p*-dimethylaminobenzenazo)phenylmercury (II) acetate in dimethylformamide and in pyridine are found to be first order⁸⁶. The rate constants at 19.4°C are $8.81 \times 10^{-5} \text{ sec}^{-1}$ in pyridine and $3.68 \times 10^{-5} \text{ sec}^{-1}$ in dimethylformamide. The free energy, enthalpy and entropy of the *cis* to *trans* change in pyridine were calculated to be $\Delta F^\ddagger = 22.5 \text{ kcal mole}^{-1}$; $\Delta H^\ddagger = 19.6 \text{ kcal mole}^{-1}$; and $\Delta S^\ddagger = -9.9 \text{ e.u.}$; in dimethylformamide the data are: $\Delta F^\ddagger = 23 \text{ kcal mole}^{-1}$; $\Delta H^\ddagger = 18.9 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -14.0 \text{ e.u.}$ The rates of ring closure of various 1,3,3-trimethylindolino-benzopyrylospirans follow a first-order law⁹². Typical rate data are given in Table 6.

4 PROPERTIES OF SOLIDS EXHIBITING PHOTOTROPY

4.1 *Exciting radiation and colour changes*

The exciting radiation which causes the phototropic change in solids generally lies in the ultra-violet frequency of $280\text{ m}\mu$. The spectral spectrum. There has been one paper in which it has been reported that strontium cyanoplatinate is activated by X-rays¹⁷⁵.

Only general statements can be made concerning the exciting radiation in the phototropic change. The spectral sensitivity of cinnamaldehyde semicarbazone has been studied⁴⁶ and found to have a characteristic ultra-violet frequency of $280\text{ m}\mu$. The spectral sensitivity of zinc sulphide^{138,140}, the succinic anhydrides ("fulgides")⁸⁸, tetrachloro-1(2)-naphthalenone^{38,59}, certain anils³, hydrazones⁸⁸, osazones^{176,177}, and stilbene derivatives⁵³ has been investigated. A recent study by Lindemann¹⁷⁸ showed that salicylidene-*m*-toluidine is yellow and crystalline in its dark-stable form but is converted to the orange-red, unstable form by irradiation with a wavelength of $365\text{ m}\mu$. Clark and Lothian⁷⁵ found that 2-(2',4'-dinitrobenzyl)pyridine gave a phototropic effect when irradiated with plane-polarized radiation of $365\text{ m}\mu$ parallel to the β (rose-pink colouration) or γ (blue colouration) directions in the crystal. The same irradiation along the α direction gave no colouration. None of the three principal directions of observation shows large absorption in the visible but there is a distinct pleochroism in the ultra-violet.

Weigert⁵⁹ found the most prominent face of the orthorhombic colourless crystals of tetrachloro-1(2)-naphthalenone is the prism (110), whose edges are parallel to the c -axis. The crystal axes of the solid are $a:b:c = 0.725:1:0.504$. The compound assumes a red-violet colour when white light falls on it, and loses this colour when placed in the dark or irradiated with yellow-green light. Using plane polarized light, Weigert found that the electrical vector in the direction of the c -axis absorbs at $375\text{ m}\mu$ and $395\text{ m}\mu$ whether the crystal is clear or excited. With the electrical vector in the ab -plane, absorption was found only at $420\text{ m}\mu$ in the clear crystal while a strong additional band appeared in the yellow-green when the crystal was excited. Using violet

light of equal intensity, stronger excitation was obtained with the electrical vector parallel to the c -axis than when in the ab -plane in spite of the greater absorption in the latter case. The "clearing up" effect of the yellow-green light is found only when the electrical vector lies in the ab -plane.

With tetrachloro-1(2)-naphthalenone it can be seen that the phototropic colour change is most pronounced along the axis which lies parallel to the edges of the prism faces. Light shining in any direction may bring about the phototropic change, but white light is most effective in promoting the phototropic change when it shines in the ab -plane and not along the c -axis. This behaviour can be explained by the fact that the wavelengths of light which are absorbed by the phototropically induced absorption band have the effect of causing this absorption band to disappear⁸⁸. In addition, the crystals are pleochroic.

Pleochroism is exhibited by anils³, succinic anhydrides^{38,179}, hydrazones¹⁸⁰, osazones¹⁸⁰ and tetrachloro-1(2)-naphthalenone¹. The colour change in some of these crystals is not uniform throughout the crystal but takes place only where the light impinges on the crystal^{13,140}. Observations have shown that the colour change in the anils¹⁹, the succinic anhydrides³, and tetrachloro-1(2)-naphthalenone⁵⁹ is not accompanied by distortion of the crystal.

If a phototropic substance is coloured by exposure to light and then dissolved, the colour disappears immediately and the resulting solution appears to be identical with that of the original compound which had not been exposed. Such solutions are non-phototropic^{1,3,21,181}.

4.2 *Reversing radiation*

This type of radiation refers to that needed to revert the excited phototropic substance back to the original or stable form. This opposing action of light of different wavelengths upon phototropic substances was discovered by Stobbe^{38,175} in his study of the succinic anhydrides. This general phenomenon is that light absorbed by the light induced absorption band of the phototropic substance has the tendency to reverse the action of the exciting light and thus cause the absorption band to disappear.

White light is reported to have a reversing

action of the following classes of compounds: anils^{53,176,177}, succinic anhydrides^{38,54}, stilbene derivatives³, and tetrachloro-1(2)naphthalenone⁵⁹. Whether the hydrazones and osazones show this effect is somewhat doubtful^{38,53}. Some quantitative data on the effect of reversing radiation on the anils^{53,176,177} and tetrachloro-1(2)naphthalenone⁵⁹ are available. The speed of the reverse change varies greatly from one compound to another and not enough quantitative data are available to draw conclusions even within a given class of compounds.

The reversing radiation for phototropic processes is of the same or longer wavelength than the radiation which originally excited the phototropic change. In most cases the maximum wavelength of the reversing radiation is of longer wavelength than the radiation which exerts the maximum exciting effect^{3,53,138,175}. However, only careful studies of individual crystals such as those by Weigert⁵⁹ and by Clark and Lothian⁷⁵ could give accurate data on this question.

4.3 Influence of surrounding atmosphere on phototropy

Not much can be said about the influence of a surrounding atmosphere on phototropism for the observations reported in the literature are often conflicting. However, the following phototropic processes in the solid state have been described as dependent upon the atmosphere surrounding the solid.

(1) Hexanitrodiphenylamine requires an oxygen-containing atmosphere to exhibit phototropy³.

(2) Sodium 4,4'-diacetamido-2,2'-stilbene-disulphonic acid exhibits phototropy only in an atmosphere of oxygen; Stobbe and Mallison⁵³ suggest that the phototropic substance catalyses the conversion of some of the oxygen to ozone.

(3) Tetrachloro-1(2)-naphthalenone and the osazones have been tested for phototropism in vacuum, in air, in oxygen, in hydrogen, and in carbon dioxide. All of the compounds tested were found to be phototropic under the different conditions. With the osazones, phototropy was slightly inhibited by an oxygen atmosphere³.

(4) Certain anils, succinic anhydrides and hydrazones are reported to be phototropic in

air, oxygen, hydrogen and carbon dioxide but not in a vacuum³. The presence or absence of moisture in the surrounding atmosphere seems to have very little effect upon the phototropy of these and certain other substances^{3,53}.

(5) Oxygen is said to be necessary for a reversible colour change of methylene blue in a gelatin film. In the absence of oxygen the bleaching is more rapid than in an oxygen atmosphere but the colour will not return in the dark¹⁸².

(6) According to a number of authors, lithopone shows phototropism only when exposed to light in the presence of moisture; it requires the presence of oxygen in order to undergo the reverse change in the dark^{9,11,140,143}. Ammonia, formaldehyde, lead acetate, and other reducing agents have been reported to increase the light sensitiveness of lithopone^{138,140,143}.

4.4 Mixtures

4.4.1 Organic mixtures

Padoa³⁵ tested mixtures of a phototropic substance and a non-phototropic substance in solid solutions. He found that benzalphenylhydrazone (phototropic) with a little diazoaminobenzene (non-phototropic) is phototropic; for example, solid solutions of the hydrazone containing 1.6 per cent diazoaminobenzene were phototropic while a 5 per cent diazoaminobenzene concentration was non-phototropic. Anisylidene-benzylamine (non-phototropic) in a concentration of 1% in anisalphenylhydrazone (phototropic) is phototropic. In the cases studied by Padoa, it was found that mixed crystals show the same phenomenon on prolonged exposure to light as the pure hydrazone, that is, the system becomes colourless and is no longer affected by light. In addition, the adulterant causes the dark change to take place more rapidly than with the pure hydrazone.

4.4.2 Amorphous mixtures

Stobbe³ reported the phototropic behaviour of anils, succinic anhydrides, hydrazone, osazones and stilbenes mixed with various resins. Phototropic behaviour was often observed depending on whether the mixture was prepared by warming the constituents together or by

precipitating them from solution. In some cases reverse phototropism was observed as with benzalphenylhydrazone in "metastrol" where the effect of light was to cause the colour of the dark stable modification to fade. There seems to be no general method of predicting whether a mixture will be phototropic, even though one of the components of the mixture is phototropic. In some systems in which phototropy was exhibited by the mixture there was clearly some crystallization of the phototropic substance.

Cotton, silk and wool were stained with anils and succinic anhydrides by Stobbe^{3,54}. These stained fabrics are phototropic but their colour reaction to light is not as strong as that of the pure substances. Stearns¹⁰⁵ reported the phototropic behaviour of *Calcocid Milling Yellow O* on wool, *Calcosol Yellow G* on cotton and *Calcodur Yellow 4GI* on nylon.

4.5 Fatigue

It can be generally stated that solids exhibiting phototropism show fatigue. The readiness with which phototropic substances fatigue varies markedly. Anils^{18,24}, benzalphenylhydrazone¹¹, and some of succinic anhydrides^{3,38,54} are reported to fatigue very quickly; lithopone⁸ and $\text{HgI}_2 \cdot 2\text{HgS}$ ¹²⁵ are supposed to show fatigue. The anils fatigue to a darker modification; the other substances fatigue to a modification as light in colour, or lighter than the original dark, stable form. The excited colour of the compound slowly deteriorates with continued exposure and finally the colour fades until it is even less pronounced than the colour of the original dark form. In contrast, salicylidene-*m*-toluidine retains its photoreactive properties unimpaired after a month¹⁹.

Some substances evidently undergo a pronounced chemical change in the fatigue process, e.g., diphenylsuccinic anhydride and triphenylsuccinic anhydride^{3,38,54}. Other substances may fatigue readily and yet not suffer any measurable chemical change, e.g., benzalphenylhydrazone¹¹. Benzalphenylhydrazone loses its phototropic property on long exposure to exciting radiation and if the crystals are broken in a mortar, the sample regains its phototropic properties¹⁸¹. The complex formed by the reaction between a fluorescent pigment and albumin degenerates with repeated exposure¹⁰⁴.

4.6 Influence of temperature on the phototropic process

The concern of this section is limited to the influence of temperature on the phototropic process and no effort is made to discuss the phenomenon of thermotropy. In the phototropic change the temperature influence can be manifested in two distinct ways: it causes a change in the phototropic material so that the radiation that induces the phototropic change is of a different wavelength than that affecting the non-heated sample; and it influences the rates at which the light-induced phototropism and the reverse change take place.

Colour changes with temperature are shown both by inorganic compounds¹¹⁶ and organic compounds (see also ref. 18, 19, 21, 23, 24, 38, 63, 183-187). It can be said generally that an increase in temperature causes a shift of the excitation energy to longer wavelengths and *vice versa*. Some compounds are known that show phototropy only at low temperatures. For example, salicylidene-*p*-anisidine and 2-hydroxy-3-methoxybenzylidene-*p*-xylylidine show phototropy only at -20°C ⁵⁷. Another example is that of α -anisyl- γ,γ' -diphenylsuccinic anhydride which is completely excited by light of a wavelength longer than $297\text{ m}\mu$ when it is above 22°C , while below -35°C , under the same conditions of illumination, it is not excited by light whose wavelength is greater than $297\text{ m}\mu$ ³⁸. Stobbe^{38,53} has collected similar information on other succinic anhydrides, hydrazones and stilbene derivatives.

Padoa and his co-workers^{176,177,180,188,189} have studied the influence of temperature on the rates with which phototropic substances change their colour. Their method of study was to prepare for each phototropic substance two different colour standards which correspond to two different colours exhibited by the compound at different stages of excitation. The time required for each mixture to reach a definite colour when the illumination was constant was determined at different temperatures. In other words, when defined in terms of time at constant illumination, the temperature coefficient represents the time required for a definite colour change divided by the time required for the same colour change after the temperature of the substance has been raised 10°C . Table 7 contains a summary of some

of the work by Padoa and his co-workers. Unless otherwise specified, white light was used for the study. When filtered light is used the temperature coefficient varies with wavelength as predicted by Trautz¹⁹⁰.

Padoa *et al*¹⁸⁸ found that the transformations of solid salicylidene- β -naphthylamine and of benzalphenylhydrazone in light follow first-order kinetics and that the thermal reverse process is second-order. As one can see from Table 7 the temperature coefficients for many phototropic changes are of the order exhibited by photochemical reactions.

tion of Hg(HS)CNS is unaffected by temperature while Hg(I)CNS has a temperature coefficient of 1.05 at 40° to 50°C and 1.2 from 50° to 60°C. The reverse or dark reactions for both compounds have temperature coefficients of approximately 2. Rao and Watson questioned whether or not their experimental procedures were correct since they reasoned the dark reactions should have a temperature coefficient of about 1 which is characteristic of a purely photochemical reaction. Since the compounds under study were difficult to prepare the presence of impurities and their in-

Table 7 TEMPERATURE COEFFICIENTS OF PHOTOTROPIC REACTIONS

Substance	Reaction in dark	Reaction in light	Reference
Benzalphenylhydrazone			
white light	1.7	1.07	38, 188, 189
blue light		1.08	177
violet light		1.04	177
Benzil- <i>o</i> -tolyllosazone			
white light		1.05	177
blue light		1.12	177
Diacetamidostilbenedisulphonic acid	1.65	1.21	176
Piperil- <i>o</i> -tolyllosazone	2.0	1.06	189
Salicylidene- β -naphthylamine	2.0	1.47	188
Triphenylsuccinic anhydride			
blue light		1.29	177
green light		1.67	177
yellow light	0.89		177
red light	1.08		177

The objection to Padoa's technique for determining the temperature coefficient is that while the phototropic substance is being excited by light, the dark reaction is also going on thereby retarding the light reaction. In addition, a decrease in temperature slows up the dark reaction much more than it does the light reaction; therefore, the retarding influence of the dark reaction is relatively decreased. The experimental results for the temperature coefficient would therefore appear to be smaller than they actually are. From a practical point of view, this objection is of little importance since the absolute rate of the light reaction is usually much greater, even at ordinary temperatures, than the rate of the dark reaction.

The compounds Hg(HS)CNS and Hg(I)CNS were studied by Rao and Watson¹²⁰ for influence of temperature on the phototropic phenomenon. The velocity of the transforma-

fluence on the phototropic processes cannot be neglected. However, their value for the dark reaction compares favourably with those of Padoa *et al* for piperil-*o*-tolyllosazone. More studies are needed in this area of the phototropic phenomenon.

Tanaka¹¹⁹ has reported that calcium titanate can be converted from its violet colour (excited form) to white by heating to about 220°C. However, MacNevin and Ogle¹¹⁸ reported that the violet colour was retained until a temperature between 360° and 400°C was reached. For barium titanate the colour disappeared between 220° and 270°C. These same authors reported that when the samples were heated during exposure to ultraviolet light a temperature between 480° and 610°C was needed to prevent entirely the development of colour in both calcium and barium titanate.

Another way to assess the effect of tem-

perature on the phototropic process is to consider the increase in intensity of light required to hold a phototropic substance to a given colour while the temperature is raised^{138,180}. Salicylidene- β -naphthylamine requires an increase in light intensity of 40 per cent for each increase of 10°C in temperature, while benzal-phenylhydrazone requires the light intensity to be increased 70 per cent for each 10°C¹⁸⁰.

Since the speed of the dark reaction increases much more rapidly with temperature than that of the light reaction, there should be a temperature at which the dark reaction becomes so rapid that observable phototropic change does not occur. In other words, the energy required to maintain even the slightest colour change in a phototropic substance becomes enormously great. Senier and his co-workers have studied this property in some of the phototropic anils. Data from their work are summarized in Table 8. Similar data on certain succinic anhydrides, hydrazones, osazones and stilbenes have been collected by Stobbe and his co-workers^{3,38,53}.

states of a phototropic substance but quantitative data are lacking. Questions that arise concerning the difference in energy content of the normal and excited form are (1) how much more energy is possessed by the excited than the normal form of the substance and (2) in what form is the energy released when the excited state decays? The information summarized below appears to be the only information available on energy relationships.

4.7.1 *Heats of combustion*

The data on heats of combustion are summarized in Table 9. The differences in the heats of combustion are so small that it is doubtful if they are larger than the experimental error of the determinations. Further experiments, using modern calorimetric methods, are desirable.

Two rather interesting reports of change in melting point with phototropic change have been reported¹⁹². Benzal-*o*-tolylhydrazone was reported as having a melting point of 100°–102°C for the stable form and 80°–83°C for

Table 8 TEMPERATURE EFFECTS OF PHOTOTROPY IN ANILS¹⁹

Anil	Higher temperature limit, °C
Disalicylidene- <i>m</i> -phenylenediamine (needles)	75
Disalicylidene- <i>m</i> -phenylenediamine (plates)	30
2-Hydroxy-3-methoxybenzilidene-1,2,5-xylydene ...	Between room temperature and —20
Salicylidene- <i>p</i> -aminobenzoic acid	Approx. 20
Salicylidene aniline	50.5 (melting point)
Salicylidene- <i>o</i> -anisidine	30
Salicylidene- <i>o</i> -bromoaniline	65
Salicylidene- <i>p</i> -bromoaniline	48
Salicylidene- <i>o</i> -chloroaniline	82–83 (melting point)
Salicylidene- β -naphthylamine	Between 110 and 126
Salicylidene- <i>m</i> -toluidene	39.5 (melting point)
Salicylidene-1,3,4-xylydene	76 (melting point)

Brickwedde¹⁸⁸ found, in contrast to the behaviour of organic compounds, that the rate of darkening of zinc sulphide is not greatly affected by increasing temperature.

Apparently no effort has been made to correlate the critical temperature at which phototropism ceases with any other properties of phototropic substances.

4.7 *Energy differences between normal and excited states*

It is believed by some investigators that there is a difference in the energy content of the normal (in dark environment) and the excited

the excited form. Benzal-*p*-tolylhydrazone is reported to change in melting point from 114°C in the stable form to 101°C in the excited form.

4.7.2 *Exposure of photographic plate*

Some investigators, e.g., Gallagher¹⁹³, have reported that they could observe energy released from the excited form as it decayed to the dark form by allowing the "radiant energy" from the excited form to impinge on a photographic plate. Their findings are not very convincing, and the observations are more characteristic of the Russell effect^{194–196}, al-

though chemical fogging cannot be ruled out.

Zanella¹⁹⁷ observed fogging of a photographic plate by both the stable and the excited forms of benzalphenylhydrazine; Venkataramaiah and Janakiram¹⁹⁸ made similar observations on $\text{HgI}_2 \cdot 2\text{HgS}$, Hg(I)CNS and Hg(HS)CNS , and both sets of results seem to be clear examples of the Russell effect. The succinic anhydrides³⁸ and cinnamaldehyde semicarbazone⁴⁶ did not produce an image on a photographic plate. Stilbene derivatives chemically fog a photographic plate but gave no evidence of emitting light.

Table 9 HEATS OF COMBUSTION OF PHOTOTROPIC SUBSTANCES

Substances	Heat of combustion		Difference	Reference
	Normal cal/g	Excited cal/g		
Benzalphenylhydrazine	8668.8	8669.1	0.3	191
Salicylidene- β -naphthylamine	8291.5	8294.4	2.9	191
Triphenylsuccinic anhydride	7810.4	7816.9	6.5	3

4.8 Magnetic susceptibility

Bhatnagar *et al.*^{15,199} carried out magnetic susceptibility studies on both the stable and excited forms of certain anils and hydrazones and found that neither of the forms showed paramagnetism, and a similar conclusion was reached by Singh and Datt⁶⁵ in respect to a large number of phototropic substances.

p-Dimethylaminophenyliminocamphor and *p*-diethylaminophenyliminocamphor are diamagnetic when they are first prepared but become paramagnetic after exposure to light. Singh and Datt⁶⁵ attribute this change either to polymerization or to formation of free radicals, more probably the latter.

The magnetic susceptibility of tetrachloro-1-(2 or 4)-naphthalenone has been studied²⁰⁰ and found to have a value of -5.1×10^{-6} after 20 minutes exposure to light as compared to a limiting value in the dark of -135×10^{-6} . The phototropism of this compound was attributed to the formation of free radicals or to triplet states.

When HgI_2 and HgS are heated together they form a system whose composition has been defined as $\text{HgI}_2 \cdot 2\text{HgS}$. This system is yellow in the stable form but black in the excited form. It has been reported by Takei¹⁸⁷ that the excited form of this system is paramagnetic whereas the original mixture of the two compounds before heating is diamagnetic.

4.9 Photoelectric effect

There have been only a few studies on the photoelectric effect as related to phototropism^{175,193,201,202} and no real agreement as to a possible relation between these phenomena has yet been reached.

4.10 Kinetics in solids

The transformation of the excited form of salicylidene- β -naphthylamine to the stable form was shown by Padoa and Minganti¹⁸⁸ to be a second-order reaction. For benzalphenyl-

hydrazine the dark reaction was also second-order and the light reaction first-order. An equilibrium of the kind $A_2 \xrightleftharpoons[\text{dark}]{\text{light}} 2A$ was proposed. The dark reaction for salicylidene-*m*-toluidine has been described as first-order¹⁷⁸ and the activation energy is reported as 25 kcal mole⁻¹.

Takei²⁰³ made measurements on the velocity of the phototropic reaction of $\text{HgI}_2 \cdot 2\text{HgS}$ and that of the reverse reaction promoted by heat. The phototropic reaction at low temperatures is unimolecular and the velocity constant is nearly the same at -50° and 5°C indicating that the reaction is purely photochemical. At higher temperatures, owing to the reverse reaction, the apparent velocity constant decreases. The velocity constant of the reverse reaction varies linearly with $1/T$ at temperatures above 50°C . The energy of activation was calculated as 12.8 kcal mole⁻¹ at 26° and 36°C , the observed values deviating from linearity possibly owing to catalysis by oxygen.

4.11 Other important measurements

Few data are available on quantum yields of phototropic processes. On the assumption that more than 2% conversion of salicylidene-*m*-toluidine takes place on irradiation with 365 $\text{m}\mu$ radiation, the quantum yield is higher than 1¹⁷⁸; if conversion is complete the yield is of

the order of 100. Clark and Lothian⁷⁵ could not determine the quantum efficiency in the phototropic behaviour of 2-(2',4'-dinitrobenzyl)pyridine but did determine Qf (where Q = quantum efficiency and f = oscillator strength of the induced absorption band). Along the β -direction of the crystal $Qf \geq 0.5$ and along the γ -direction $Qf \geq 0.10$.

Takei¹²⁸ has reported the electrical conductivity of $\text{HgX} \cdot 2\text{HgS}$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) to be about $10^{-10} \text{ohm}^{-1} \text{cm}^{-1}$ at 50°C and $10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ at 150°C . The conductance is in the order $\text{Cl} < \text{Br} < \text{I}$. The heat of activation of $\text{HgX}_2 \cdot 2\text{HgS}$ is 32, 23 and 22 kcal mole⁻¹ for Cl, Br and I, respectively¹²⁸.

The calculated enthalpy increase from the dark to the excited form of salicylidene-*m*-toluidine corresponds to not more than 5% of the absorbed energy¹⁷⁸.

The electron spin resonance (ESR) of several phototropic solids has been measured by Gutowsky, Rutlage and Hunsberger²⁰⁴. The only compound showing any ESR absorption was N-(3-pyridyl)syndone and it is doubtful if the ESR absorption is really due to the particles which account for the phototropism. The absorption peak is a simple bell-shaped curve with no resolvable hyperfine structure.

Hayashi, Maeda, Shida and Nakada²⁰⁵ measured the ESR on a substance prepared from the oxidation of 2,4,5-triphenylimidazole with potassium ferricyanide. The structure of this substance, which is phototropic, has not yet been established. The ESR absorption was measured on the first derivative curve and gave a single peak with no structure; the compound showed ESR absorption in both the solid state and in solution. The spin concentration of a 0.1% solution in benzene was about 10^{18} spin cc⁻³ immediately after irradiation by direct sunlight. The rate of decay was found to be first-order. The activation energy between 15° and 60°C is reported as 14 kcal mole⁻¹ and the ΔH of the reaction as -5 kcal mole⁻¹.

5 EXPLANATIONS OF THE PHOTOTROPIC PHENOMENON IN SOLIDS

There is no one explanation which will account for the mechanism involved in all phototropic

changes. In the descriptions which follow an effort has been made to summarize those explanations which have been well established or seem to be feasible in light of the evidence available. The discussion will be divided into consideration of inorganic and organic compounds.

5.1 Inorganic compounds

5.1.1 Alkaline earth metals

MacNevin and Ogle¹¹⁸ reported that the occurrence of phototropy in barium and calcium titanate is dependent upon the octahedral structure of these compounds, and also that an impurity such as Fe^{3+} , Zn^{2+} , V^{5+} , or Sb^{5+} must be present. They found that the phototropic effect increases with the amount of impurity. Magnesium titanate, which has the cubic close-packed structure, does not show phototropism, even in the presence of impurities. Thus MacNevin and Ogle attribute the presence or the lack of phototropism to the geometry of the structure.

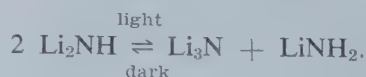
5.1.2 Copper(I) halides

Hecht and Miller¹⁴⁸ concluded that the phototropy of copper(I) chloride was due to disproportionation, and that the metallic copper so formed was present in an unstable form:



5.1.3 Lithium imide

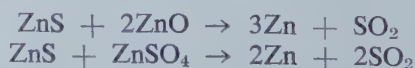
Dafert and Miklausz¹⁵¹ proposed that the mechanism of the phototropic change in lithium imide could be represented as follows:



Lithium nitride is brown and is known to react with lithium amide as indicated by the dark reaction.

5.1.4 Lithopone

Cawley¹¹ suggested that blackening in lithopone was due to the formation of metallic zinc as follows:

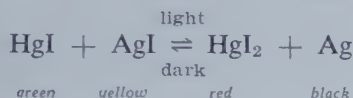


Evidence to support Cawley's view is found in the observation by a number of wor-

kers^{9,138,140,142,143} that oxygen is needed for the bleaching of the blackened lithopone. Brickwedde¹³⁸ suggested that the zinc sulphide in lithopone was converted into metallic zinc and hydrogen sulphide by the action of light in the presence of moisture, while Lenard¹⁴⁰ considered that the zinc sulphide in lithopone was converted into zinc and sulphur by action of the light. It is obvious that there is, as yet, no satisfactory explanation for the phenomenon of phototropy in lithopone. It is doubtful if "lithopone" as marketed today exhibits phototropism.

5.1.5 Mercury compounds

It has been proposed¹²⁹ that the mixture of silver iodide and mercury(I) iodide formed by toning a silver photographic plate with mercury(II) iodide undergoes the following reaction:



Rao *et al*²⁰⁶ suggested that dithiotrimercury (II) salts of the general formula $2\text{HgS} \cdot \text{HgX}_2$ are dissociated by light forming black HgS and HgX_2 (where X = anion of a monobasic or dibasic acid). Takei^{121,126,128,187,203,207} has made an extensive study of the system $2\text{HgS} \cdot \text{HgI}_2$. This system is dark violet and, if heated at 170°C , it becomes yellow and phototropy appears. In his first paper¹⁸⁷, Takei proposed that the black powder formed by the action of light on $2\text{HgS} \cdot \text{HgI}_2$ is not a mixture of HgI_2 and HgS since the mixture is diamagnetic whereas the phototropic $2\text{HgS} \cdot \text{HgI}_2$ on exposure to sunlight becomes paramagnetic. Furthermore, X-ray studies¹²⁶ showed no difference in crystal structure between the dark and excited forms.

Microscopic observation of a single crystal of $2\text{HgS} \cdot \text{HgI}_2$ after excitation showed many black spots which Takei attributed to colloidal mercury¹²¹. Heat accelerates the return from the activated to the stable (yellow) form of the complex and this has been explained by Takei as due to the vaporization of the mercury at elevated temperatures. Also, Takei suggests that the neutral atoms, sulphur and iodine, remain behind as the mercury vaporizes and reach the surface by thermal diffusion.

He proposes further that some of these atoms combine with mercury to form HgS and HgI while others in the presence of air and moisture form sulphate, sulphite and iodide ions¹²⁸.

Takei has extended this study of mercury compounds to include Hg(X)CNS (where X = halogen) and has explained the phototropy as due to the decomposition of these complexes into colloidal mercury²⁰⁷. The magnetic susceptibility of these compounds does not return to the original value after passing through the phototropic cycle. Takei explains this by supposing that the Hg(X)CNS decomposes into its components with the simultaneous formation of a positive hole in the crystal when an electron belonging to the molecule is raised to the conduction band.

5.1.6 Rutile and synthetic titanium dioxide

Weyl and Forland¹³⁵ concluded that when light strikes an impurity ion, for example Fe^{3+} , in a titanium dioxide lattice, an electron from the foreign ion is excited and either moves into an oxygen vacancy of the defective rutile structure thus producing an Fe^{4+} ion or attaches itself to a Ti^{4+} ion to give coloured Ti^{3+} . For low concentration of iron these investigators assumed that the electron transfer is from Fe^{3+} to Ti^{4+} ²⁰⁸.

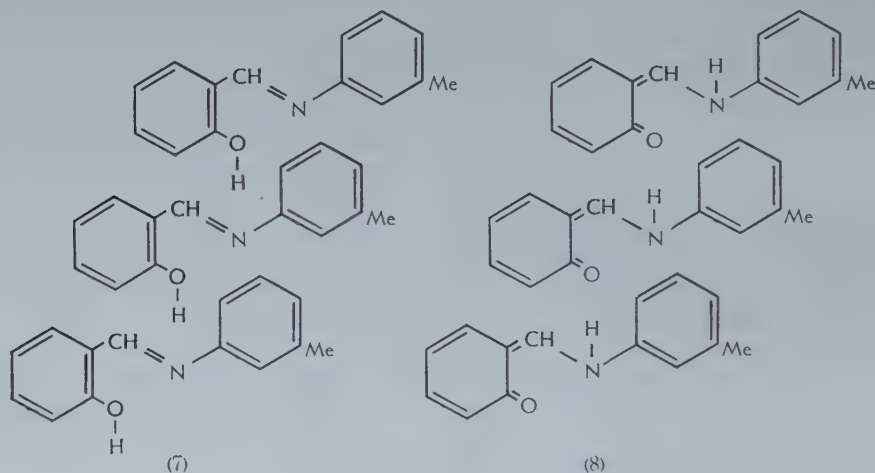
Recently McTaggart and Bear¹³⁶ prepared pure TiO_2 from the vapour-phase oxidation of TiCl_4 which showed no phototropic effects. Starting with anatase in the presence of Fe^{3+} , they found that the colour change bore an inverse relationship to the percentage of rutile present. McTaggart and Bear propose that the phototropic properties of titanium dioxide can be explained as follows. The impurity in rutile is at the surface and the nature of the bonding is such that the stable form is a reduced form of the impurity. An oxygen-containing atmosphere is necessary for the phototropic process to take place. On cessation of irradiation the higher valence form of the ion reverts to the lower form. Rapid reversal of colour obtained when irradiated samples are heated to a relatively low temperature may be the result of activation in which the change of valence is accelerated. The presence of water plays a decisive part in the process.

McTaggart and Bear suggested that if their

mechanism to explain phototropy of titanium oxide is correct, then other host oxides besides TiO_2 would show phototropism. They studied¹³⁷ a number of white oxides (Nb_2O_5 , Al_2O_3 , ZnO , HfO_2 , ThO_2 , SnO_2 , Ta_2O_5 , ZrO_2 , BeO , GeO_2 , SiO_2 , and MgO) which were contaminated with oxides of metals such as iron, chromium and manganese. In general, they found the phototropic colour change to be from off-white (stable) to pale grey (excited).

5.2 Organic compounds

It would appear that most phototropic processes in organic compounds are due to mesomerism, isomerism, free radical formation or molecular aggregations. These ideas are outlined below.



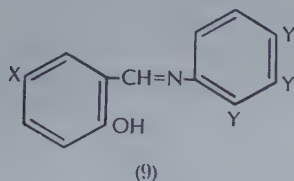
5.2.1 Anils

Senier and Shephard¹⁸⁶ and Senier, Shephard and Clarke¹⁹ proposed that the colour change in anils was due to a change in aggregation. They reasoned that whatever the change, it involved a small energy difference because of the ease with which it took place. By crystallization from concentrated solutions, they prepared a red modification of salicylidene- β -naphthylamine which appeared to be identical with the phototropic form prepared by light⁵⁰. Magnetic susceptibility data by Bhatnagar and Kapur¹⁹⁹ support this interpretation. Also, de Gaouck and Le Fevre²⁵ concluded that the phototropic mechanism of anils consisted of a mutual interaction of molecules in the lattice

and not in some rearrangement undergone by the molecules. de Gaouck and Le Fevre proposed the structural relationships (7) and (8) to explain the phototropy of solid salicylidene-*m*-toluidine. The proposed crystal lattice arranged as below has the hydroxyl hydrogen of one molecule near the nitrogen atom of another. The authors explain that the solid then is a hybrid between forms (7) and (8) in which the formulae represented here are images in parallel planes, one over the other. Form (7) represents the stable form of the anil and form (8) represents the ortho-quinoid structure which is red or yellow, depending on the anil. The authors report the heat of formation of the covalent links in form (8) is 15 kcal mole⁻¹ greater than in form (7).

de Gaouck and Le Fevre suggested that if their structure for salicylidene-*m*-toluidine is correct then substituents added to the molecule which alter the hydrogen bond resonance would affect phototropic behaviour; *ortho*- and *para*-hydroxyanils should lose their phototropism if the hydroxylic hydrogen is blocked by methylation. In a study of substituted compounds of the general structure (9), if X is any group other than hydrogen the compounds are always non-phototropic regardless of the nature of Y. If X is hydrogen and the ring containing Y is *m*-toluidine, aniline or *p*-bromoaniline, phototropism is present in the anil. de Gaouck and Le Fevre concluded that no substituent should be present in the

molecule which reduces the electron density on the nitrogen atom.



Recently Lindemann¹⁷⁸ has supported the hydrogen-bonding interpretation of phototropic phenomenon of anils. He attributes the colour change to the conversion of the intramolecular hydrogen bonds between the OH and —CH=N— groups in the yellow form of salicylidene-*m*-toluidine into intermolecular hydrogen bonds between adjacent molecules to give the orange-red form.

5.2.2 Fluorescent pigments with certain proteins

Certain fluorescent pigments react with —SH compounds to give products that are phototropic¹⁰⁴. Fujimori attributes the phototropic process to the photochemical formation of pigment free radicals and $\text{RS}\cdot$ free radicals.

5.2.3 Isonicotinic acid hydrazide derivatives

Mattu, Pirisi and Manca⁶³ found that *o*-nitrobenzylideneisonicotinic acid hydrazide is pale gold-yellow in the stable form but is excited on exposure to sunlight to a red colour, and

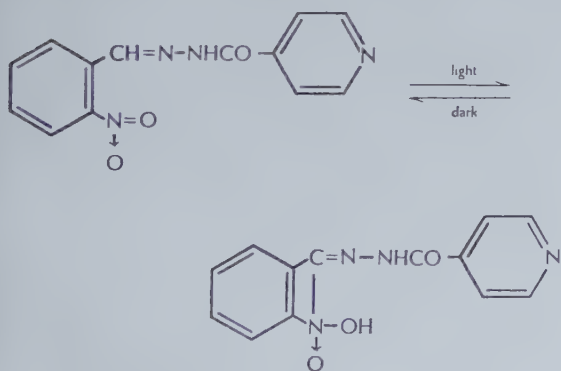


Figure 10 Colour changes in *o*-nitrobenzylideneisonicotinic acid hydrazide

on prolonged exposure, to a ruby red, and finally to a red-brown colouration. These authors reasoned that the colour change was one of equilibrium between the forms (Fig. 10).

Ultraviolet light shifts the equilibrium to the right while infrared or heat shifts the equilibrium to the left. They found that the isomerization proceeds without change of crystal form.

5.2.4 Mechanism of phototropic change in crystals of 2-(2',4'-dinitrobenzyl)pyridine

Clark and Lothian⁷⁵ support the proposal of Chitschibabin, Kuindshi and Benewolenskaja²⁰⁹ as an explanation of the phototropy of 2-(2',4'-dinitrobenzyl)pyridine. The phototropy is supposed to be due to tautomeric change of the type shown (Fig. 11), and the evidence may be summarized as follows:

(1) The induced absorption band of the

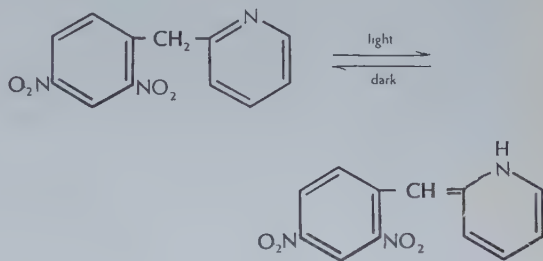


Figure 11 Phototropism of 2-(2',4'-dinitrobenzyl)pyridine

excited form in the visible region arises from the conjugation throughout the molecule.

(2) Equal bleaching rates of the induced absorptions measured with electric vectors along the β - and γ -directions suggest that both bands arise from transitions from the same absorption system in the "coloured" molecules.

(3) Bending of the $\text{CH}_2\text{—C=N}$ system could bring the hydrogen atom close enough to the N-atom for transfer to take place. Energy of such a bending vibration is likely to correspond to a thermal activation energy of 0.06 eV ($\nu = 480\text{ cm}^{-1}$) found for the colouring process.

(4) Phototropy in the solid state may be explained by the influence of the crystal lattice holding the molecule in a position where H and N atoms can approach closely enough for capture to occur, either intra- or intermolecularly.

(5) Thermal bleaching consists of the re-

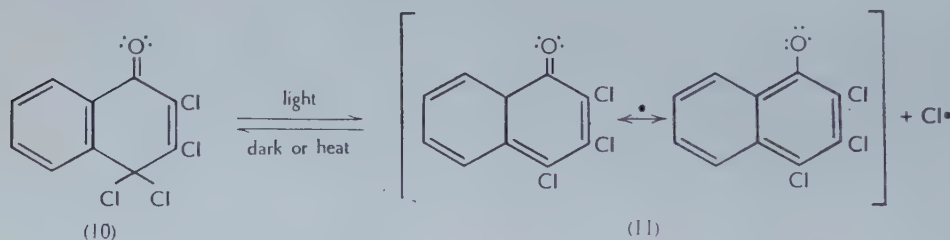
turn of the hydrogen atom to its parent atom over a potential barrier height of 0.83 eV.

(6) The first-order nature of the return of hydrogen suggests intramolecular change. It is therefore likely that the colouring process is intramolecular.

Clark and Lothian suggest that in solution or in the molten state 2-(2',4'-dinitrobenzyl)-pyridine did not show phototropy because the probability of the hydrogen jump is small due to the low energy required for rotation about the $-\text{CH}_2-$ linkage. However, more recent data^{100,101} have shown that the compound is phototropic in certain solutions (see section 3.5).

5.2.5 Quinol derivatives

The phototropy of tetrachloro-1(4H)naphthalenone (10) is attributed to the formation of naphthoxy radicals (11) through loss of chlorine atoms⁶⁰. This phototropic equilibrium is represented as follows:



Feichtemayr and Scheibe state that photodissociation is a general property of substituted quinols. The existence of the excited form (11) is shown by the photopolymerization of vinyl acetate induced by the chlorine atom or by the fading of a triphenylmethyl solution. Marckwald¹ found that of the two crystalline modifications of tetrachloro-1(2)-naphthalenone only one was phototropic and that the phototropic change involved an increase in the pleochroism of the crystals. Weigert²¹⁰ suggested that the absorption of light by the crystal causes a distortion of the electronic orbits within the phototropic crystal and that this distortion results in an anomalous absorption of light. In a latter paper, Weigert⁵⁹ extended this idea and proposed that the exciting radiation causes a widening in the distances

between the atoms of a molecule until intermolecular bonds are formed and the motions of the electrons affected by the "foreign" molecules causes the colour change. The absorption of the yellow-green rays causes a breaking of these new bonds and a return to the original state.

5.2.6 Semicarbazones

Gheorghiu^{39,50,51,211-213} has explained the phototropy of semicarbazones as an effect of mesomerism and believes that the change is due to a displacement of π -electrons, which result in the formation of one or more polar structures. He interpreted the state of the coloured molecule as being an "intermediate state" resulting from the superposition of several limited structures. Further, Gheorghiu proposed that substituents in the benzene ring capable of resonance should favour phototropy, while non-resonating substituents tend to subdue it. The semicarbazone of

$o\text{-MeOC}_6\text{H}_4\text{CH}=\text{CMeCOMe}$ is more phototropic than the semicarbazone of $\text{C}_6\text{H}_5\text{CH}=\text{CHCOMe}$, while that of $p\text{-iso-PrC}_6\text{H}_4\text{CH}=\text{CMeCOMe}$ is almost insensitive to light.

5.2.7 Stilbene derivatives

Stobbe and Mallison⁵³ proposed that stilbene derivatives on exposure to light take up oxygen to form a coloured organic oxide which may be a peroxide, an ethylene oxide, or an amine oxide. The excited material is assumed to revert to the original stilbene compound with the liberation of ozone. Stobbe and Mallison also suggested that their conclusions were supported by the results of Padoa and Zazzaroni¹⁷⁶ who concluded from the rate of colour change for the stilbene derivatives that the reaction produced by light is bimolecular.

5.2.8. Succinic anhydrides

Stobbe^{88,175} proposed that the succinic anhydrides ("fulgides") owed their colour change on exposure to light to the formation of some

kind of coloured stereoisomer. He showed that light did convert some succinic anhydrides to their stereoisomers; however, the reverse change in the dark does not appear to have been proved.

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Applications of Gas Chromatography

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1 INTRODUCTION

Gas chromatography has developed over the last eight years into one of the most important instrumental analytical techniques. Some indication of this is given by the fact that well over 1,500 papers have been published during that time, and the annual number is increasing each year. Gas-solid chromatography (GSC), with a solid adsorbent as the stationary phase, had been in use for a considerable time for the separation of gases and light hydrocarbons ($C_1 - C_4$) and was reviewed in detail by Claesson in 1946⁵³ and more recently by Janak¹⁶³. However, it was the introduction of gas-liquid chromatography (GLC) by James and Martin¹⁵⁰ in 1952 which resulted in the rapid development of the technique.

The use of a liquid stationary phase, on an inert supporting material, extended the range to include a wide variety of organic materials boiling up to above 400°C and it is with GLC that we shall be mainly concerned. Of a number of reviews and explanatory articles, mainly on GLC, the most complete review paper is that of Hardy and Pollard¹²⁵ which covers the literature up to 1958. Analytical applications have been discussed by Rose²⁷⁹ and several books on gas chromatography have been published^{16,190,256,258}.

There are three forms of GSC and GLC (see e.g. ref. 190). Elution development is generally used for analytical work since pure components are produced and the column can be used repeatedly. Displacement development may be useful for isolating a component in concentrated form, and it has recently been pointed out²⁸ that frontal analysis has advantages for the analysis of materials which "tail" in elution development. Most of the work

discussed in this review deals with elution development.

2 PRESENTATION AND COMPILATION OF DATA

In order to correlate data published by different workers and to avoid the publication of inadequate data, standard methods of data presentation have recently been recommended^{7,45,172}. Unfortunately some differences in symbolization are found in the above references, but substantial agreement has been reached on the main issues and adherence to the recommended methods should do much to avoid the ambiguities which are at present found in the literature. A separate list of symbols used in the present review is given in Section 10.

To cover the large volume of literature on gas chromatography, two abstracting services have been instituted. In England abstracts are prepared by the Gas Chromatography Discussion Group of the Institute of Petroleum Hydro-carbon Research Group, and these are circulated quarterly in book form with an index. About 2,100 abstracts have now been published by Butterworths to the end of 1959 and it is also proposed to publish an extensive collection of retention volume data. In the U.S.A., abstracts on Unisort punched cards are available from C. D. Lowry²²⁸. New abstracts are sent weekly but the cost of this service is considerably higher than for the English abstracts. The storage of retention volume data on IBM punched cards has been reported by Spencer and Johnson³⁰³.

3 SEPARATION OF MATERIALS BY GAS CHROMATOGRAPHY

3.1 Introduction

The separation of two components on a column is dependent on:

- (1) the column efficiency which determines the peak width and is measured in terms of the number (n) of theoretical plates and
- (2) the apparent retention ratio (r) which is determined by the partition or adsorption coefficients (K) of the components and the ratio of the fixed-phase to moving-phase capacity (k').

3.2 Theory of column efficiency

The theory of gas chromatography for linear isotherms, which apply with good approximation to gas-liquid chromatography, and gas-solid chromatography in some cases, has been treated in a number of papers. According to the theory the shape of an elution curve is given by a Poisson distribution which approximates to a Gaussian curve for a sufficiently large number of theoretical plates (>100). The broadening of a component band as it passes through the column is the result of a number of almost independent contributions and the net effect can be expressed by the height equivalent to a theoretical plate (HETP). Although some doubt still exists as to the correct expression for the HETP^{100,194}, it is usually given in the simplified form (derived for gas-liquid chromatography)

$$H = A + B/u + Cu \quad (1)$$

where u is the linear carrier gas velocity, and A , B , C are constants^{71,100,194} determined respectively, by packing irregularities ("eddy" diffusion), longitudinal gas diffusion, and non-equilibrium effects ("mass transfer" effects in the liquid and gas phases).

The plot of H against u is hyperbolic, as shown in Figure 1, and the minimum value of H is given by $H_{\min} = A + 2(BC)^{1/2}$ for $u_{\min} = (B/C)^{1/2}$. The effect of operating parameters on the column efficiency has been investigated in some detail (see Table 1 of ref. 125 and refs. cited below, also Glueckauf¹⁰⁵). From the above equations it can be seen that the optimum conditions for an analysis are obtained by minimizing A and BC to obtain a high column efficiency, and by maximizing B/C for short analysis times. A can be reduced by using a support of small particle size and narrow mesh range in the case of granular packed columns³¹ or by the use of capillary columns for which A is zero. C is reduced by minimizing the liquid film thickness in GLC³¹ and appears to be almost zero for GSC³³⁵. However, decrease of B by use of a dense carrier gas and high column pressure results in a corresponding decrease in u_{\min} and hence increase in analysis time^{31,68,292}. Moreover, due to the pressure drop across the column^{38,191,307} a smaller part of the column is operating near u_{\min} with a carrier gas of high viscosity and

this effect must be allowed for in the investigation of column efficiency.

In theory the minimum HETP obtainable is of the order of the particle diameter for granular packed columns and of the order of the column radius for capillary columns. Minimum values which have been reported in practice are approximately 0.3 mm³¹ and 0.1 mm⁶⁸ respectively.

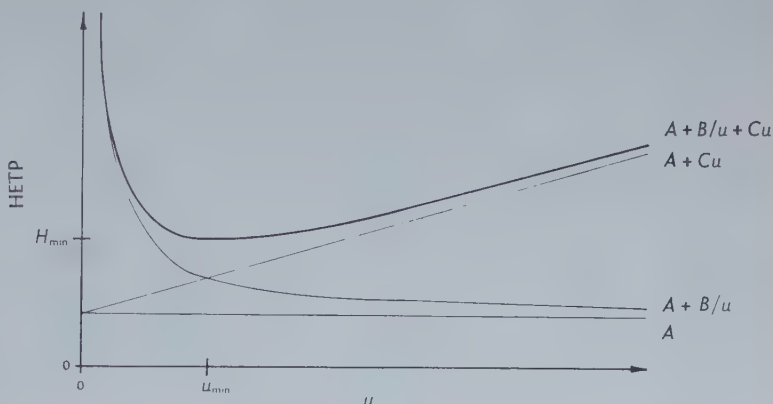
An important point which should be noted

whereas the apparent retention ratio is defined here as

$$r = (V_R)_2 / (V_R)_1 = \frac{(1 + k'_2)(1 + k'_1)}{(1 + k'_1)(1 + k'_2)} \quad (4)$$

where $k' = K(v_L/v_G)$ is the ratio of fixed-phase to moving-phase capacity. The significant difference between α and r is that α is a measure of the separation due only to the nature of the sample components and the column packing material, whereas r includes

Figure 1 Variation of HETP with linear gas velocity, u



is that the C -term⁷¹, and hence the HETP, varies with the gas and liquid diffusion coefficients and with the ratio of fixed-phase to moving-phase capacity. The HETP may therefore vary with both retention time and compound type. For granular packed columns there is generally an improvement in plate efficiency (reduced HETP) with increased retention time^{52,223,262,289,290} but the effect obtained depends²⁹² on the value of k' (see below) and for capillary columns the efficiency generally decreases with increased retention time^{68,292}.

3.3 Separation factor and apparent retention ratio

The retention volume can be expressed in the form (see Figure 2)

$$V_R = V_M + V_R' = \frac{(n/j)(v_G + K v_L) = n v_{eff}/j}{(n/j)(v_G + K v_L)} \quad (2)$$

where v_{eff} is the effective plate capacity of the column and j is the pressure gradient correction factor^{150,210}. The separation factor for two components is given by

$$\alpha = (V_R)_2 / (V_R)_1 = K_2 / K_1 \quad (3)$$

the gas holdup due to the interstitial volume of the column and detector. This contributes to peak broadening but not to peak separation.

3.4 Resolution of two components

Resolution may be defined in a number of ways but for practical purposes two methods are of particular value. The first of these is a measure of the peak height overlap, the second of the fractional band impurity. In both cases it is assumed that the peaks are Gaussian in shape. Referring to Figure 2, the peak height ratio C_1/C_2 is given by

$$C_1/C_2 = \exp\{(V_2 - V_1)^2 n / 2V_1^2\} \quad (5)$$

and this can be rearranged to give an expression for the number of theoretical plates, n , required for a given C_1/C_2 ratio

$$n = 2\{1/(r - 1)\}^2 \ln(C_1/C_2) = 2\{[1 + (1/k'_1)]/(a - 1)\}^2 \ln(C_1/C_2) \quad (6)$$

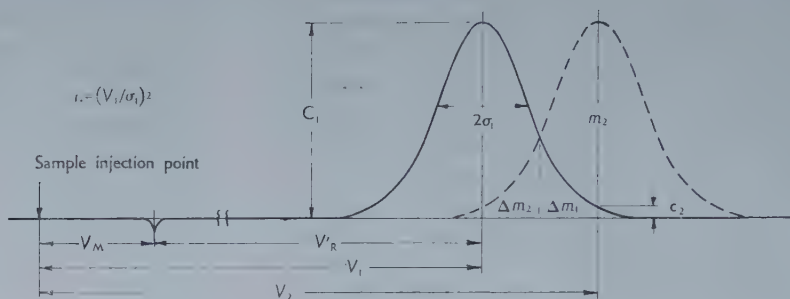
It is thus seen that a greater number of plates is required to separate two components on a capillary column (k' small) than on a granular packed column and the expression $n(k')^2/(1 + k')^2$ is a more realistic measure of the

column efficiency than n . However, unless K is small, it is easier to achieve the higher number of plates required by the capillary partly because of the low pressure drop.

When a certain purity of the separated components is required, the relation given by Glueckauf¹⁰⁴ can be used. This is based on a

to avoid variable partition coefficients and adsorption-desorption effects^{34,331} which will also distort the peak. Moreover, additional factors are required for the method of sample introduction^{190,263} and the initial distribution of solute in the liquid phase, but these effects are difficult to evaluate. Keulemans¹⁹⁰ sug-

Figure 2 Peak overlap and resolution



cut in which the fractional impurities, η , of both bands are equal, i.e. where

$$\eta_{12} = \Delta m_1 / (m_2 - \Delta m_2) \cong \Delta m_1 / m_2 \cong \eta_{21} \cong \Delta m_2 / m_1 \quad (7)$$

The result is usually given in graphical form. For two components originally present in molar proportions of m_1 and m_2 , and whose apparent retention ratio, r , is close to unity, the number of plates required to produce a given fractional band impurity can be obtained from Figure 3.

The number of plates required for the separation of two components by gas chromatography is much higher than for distillation processes, the ratio being approximately n^2 to n , since in gas chromatography only a small fraction of the total column is in use at any instant^{66,74,189}. However, the larger number of plates required for gas chromatography is more readily achieved than the smaller number required for distillation.

3.5 Instrumental factors limiting resolution

Peak distortion with consequent reduction in column efficiency may result from the sample initially occupying too large a proportion of the column. Glueckauf¹⁰⁴ and van Deemter⁶⁶ have shown that the sample volume (v_s) does not contribute to the peak width if $v_s \leq 0.5 v_{eff} \sqrt{n}$. In calculating the amount of sample to which this corresponds, it must be remembered that the initial concentration must be low

gested a constant of 0.02 for granular packed columns but for a 0.01 in. i.d. capillary column Desty⁶⁸ found that the permissible sample size corresponded to a value of less than $0.002 v_{eff} \sqrt{n}$ which amounted to about 0.1 μ g. (With capillary columns of larger diameter milligram samples have been used³⁴⁷).

Peak distortion may also be caused by too large a detector volume or by slow response of the detector and recording system. These effects have been discussed by Johnson and Stross¹⁷³, Schmauch²⁸⁵ and the author²³⁶. The effect of the overall time constant of the detector and associated recording equipment can be readily calculated. However, the effect of detector volume depends on whether or not complete mixing occurs within the detector. Results obtained in practice suggest that an intermediate situation exists, so that the correction factors derived by Johnson and Stross¹⁷³ may overestimate this effect. The safest procedure is to use equipment for which correction factors are not normally required. For symmetrical peaks this will be achieved with a ratio of approximately 30 to 1 between the (time) base-width of the peak and the overall time constant of the detector unit, and between the volume of the peak and the detector volume. It should be noted, however, that the full scale deflection time of a potentiometric recorder should not be treated as a "time constant".

4 DETERMINATION OF THERMODYNAMIC DATA

4.1 Activity coefficients from GLC measurements

Activity coefficients can be obtained from retention time measurements^{205,263} since, from Section 3.3,

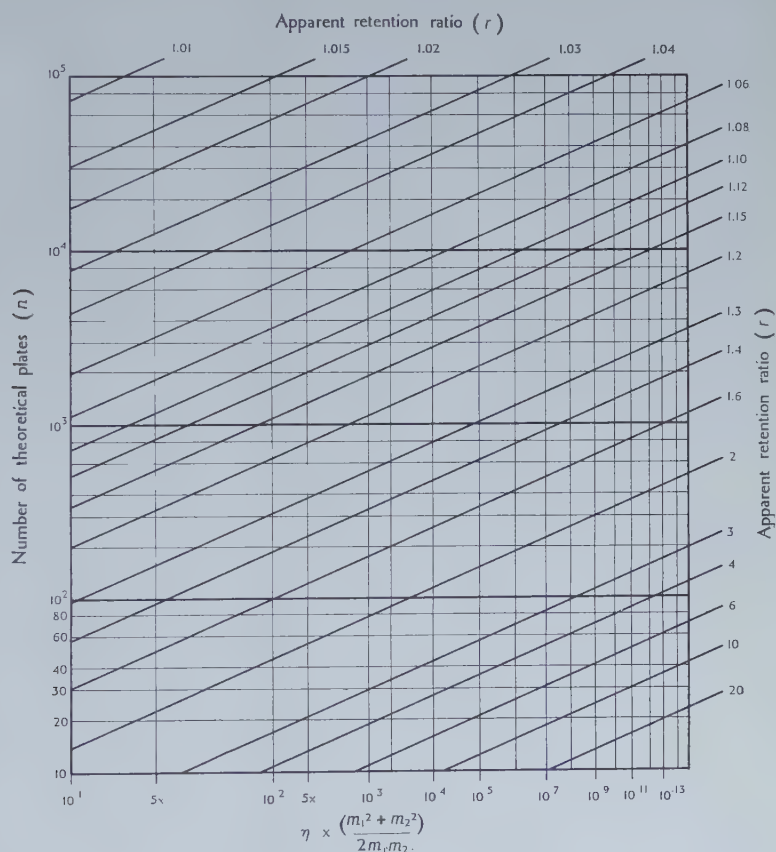
$$K = jV_R'/nv_L = V_N/V_L = \frac{M_L RT/\gamma_f p^0}{M_L RT/\gamma_p p^0} \quad (8)$$

The activity coefficients at infinite dilution, γ_f^0 and γ_p^0 , are obtained by the use of small samples or by extrapolation to zero sample size. Values determined by GLC have been

dinonylphthalate over the range 48–110°C. For both solutes, the very small temperature coefficient shows that the departure from ideality is due mainly to entropy effects.

Values of $\gamma^0 < 1$ generally occur²⁶³ only when the components are similar in polarity but differ appreciably in molecular size, or when they react chemically. At high concentrations the peak shape shows a sharp front and diffuse tail and the measured retention volume is greater than for an infinitely dilute zone. Values of $\gamma^0 > 1$ are obtained when there is a large difference in polarity between the components. The peak shape shows a

Figure 3 Fractional impurity of separated components (after Glueckauf¹⁰⁴).



found to agree well with equilibrium measurements providing that the stationary phase support is inert^{205,263}, and the method can be applied to volatile solvents by presaturating the carrier gas with the solvent²⁰⁵.

A precision of $\pm 1\%$ has been reported by Adlard, Khan and Whitham⁴ for the activity coefficients of benzene and cyclohexane in

diffuse front and sharp tail at high concentrations and the measured retention volume is less than for an infinitely dilute zone. Since the partition coefficients are low, the plate capacities will also be low.

4.2 Heats and entropies of solution by GLC

The apparent heat of solution, ΔH_s , and the

excess partial heat of solution, ΔH_s^E , can be obtained from the relationship²⁶³,

$$\partial(\ln K)/\partial(1/T) = \Delta H_s/R = -(\Delta H_v - RT - \Delta H_s^E/R) \quad (9)$$

Results²⁶³ show that ΔH_v predominates in determining the change in K with temperature and reasonable estimates of K can therefore be obtained from one determination.

The entropy of solution (ΔS) can be calculated from the heat of solution and the free energy of solution since

$$\Delta S = (\Delta H_s - \Delta G)/T \quad (10)$$

$$\Delta G = -RT \ln(273K/T) \quad (11)$$

4.3 Heats of adsorption and adsorption isotherms

The heat of adsorption, ΔH_A , can be obtained in a similar way to the heat of solution from

$$\partial(\ln K_A)/\partial(1/T) = \Delta H_A/R \quad (12)$$

and values have been obtained¹¹⁴ for low boiling gases on charcoal and light hydrocarbons on alumina and silica gel.

Adsorption isotherms have also been determined by GSC for benzene and cyclohexane on charcoal¹⁵⁵ (also entropies of adsorption¹⁵⁵) and for pentane, hexane, cyclohexane and benzene on silica gel, calcium carbonate and calcium sulphate¹¹⁵. In the case of cyclohexane on calcium carbonate the form of the isotherm was altered by adsorbed moisture.

5 ANALYTICAL APPLICATIONS OF GAS CHROMATOGRAPHY

5.1 Separation and identification of simple mixtures

As shown in Section 3 the separation of a mixture by gas chromatography is dependent on the column efficiency and the ratio of the partition or adsorption coefficients of the components. For GLC,

$$a = (V_R)_2/(V_R)_1 = K_2/K_1 = \gamma_1 p_1^0/\gamma_2 p_2^0 \quad (13)$$

$$\text{and } \log a = \log(p_1^0/p_2^0) + \log(\gamma_1/\gamma_2) = \{(\Delta H_s)_1 - (\Delta H_s)_2\}/RT \quad (14)$$

For an ideal solution ($\gamma = 1$), a will be determined by the solute vapour pressures.

On the other hand separation of close-boiling mixtures is dependent on alteration of the γ_1/γ_2 ratio by solute-solvent interaction. Thus *m*- and *p*-xylenes^{70,348} and various other close-boiling isomers can be separated on selective stationary phases and even racemic mixtures on optically active phases (e.g., ref. 178). Vapour pressure and solution effects do not always combine to enhance separation and these two cases are clearly differentiated by the use of grid-type plots as shown by Purnell²⁶⁷. Improved separation is usually obtained at lower temperatures, provided that the column efficiency is not adversely affected (see e.g., ref. 72), since $(\Delta H_s)_1 - (\Delta H_s)_2$ is generally nearly temperature independent. Also the plate capacity is increased by lower temperatures.

There is no adequate theory of the liquid state from which accurate separation factors can be calculated and it is necessary to rely on empirical or semi-empirical methods in the choice of stationary phase. A qualitative classification scheme for solutes and solvents has been put forward by Keulemans^{190,125} based on the degree of molecular interaction resulting from orientation (dipole-dipole), induction and dispersion (non-polar) forces¹⁹². Loose chemical adduct formation must be considered as a separate class and selective interaction of this type has been used for the retardation of unsaturated hydrocarbons by interaction with the silver ion^{21,55,101,294} and of other compounds, particularly amines, by various metal complexes^{13,49}. Some idea of the selectivity possible is given by the figures quoted by Barber *et al*¹³. The plate requirements to separate γ -picoline and 2,6-lutidine on *Apiezon L* and manganese stearate are given as 15,000 and 5 plates respectively.

A semi-empirical approach has been used by Pierotti *et al*²⁵⁹, based on experimentally obtained relationships between the activity coefficients and the solute and solvent structures. For a homologous series it is frequently found^{133,259} that, providing the lower members are excluded and the carbon number range is limited,

$$\log \gamma \equiv a_1 + (b_1/N')N \quad (15)$$

where N and N' are the carbon numbers of the solute and solvent respectively. Moreover

it is also frequently found that

$$\log p^0 \equiv a_2 - b_2 N \quad (16)$$

$$\text{and } \log p^0 \equiv a_3 - b_3/T \quad (17)$$

On the basis of these approximations it can be shown that a linear relationship can be expected, as is found in practice (see refs. 125, 152), between $\log V_N$ and

- (1) the number of carbon atoms in the molecule,
- (2) the logarithm of the vapour pressure of the pure solute,
- (3) the boiling point of the pure solute,
- (4) the reciprocal of the solvent temperature and
- (5) $\log V_N$ for a different solvent.

These relationships are of particular value in the identification of unknown components, and an example of types (1) and (5) is shown in Figure 4. It should be noted that the transfer

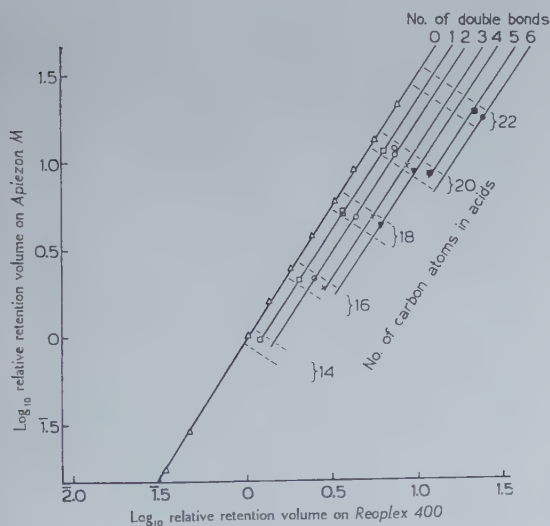


Figure 4 Log retention volume plot for fatty acid methyl esters (courtesy of Journal of Chromatography¹⁴⁹)

of retention data other than relative values from one column to another must be done on a unit volume or weight basis, since the net retention volume, V_N , is dependent on the amount of liquid phase in the column (or on the surface area in the case of adsorbents).

Similar relationships to the above are found with adsorption columns¹⁶¹ but tailing generally occurs due to surface heterogeneities. This can be overcome by the use of very

small samples or adsorbents with structureless surfaces³³⁵. The active sites which cause tailing can be deactivated by adding a small percentage of liquid phase to the column^{83,84,161} or by adding a strongly adsorbed vapour to the carrier gas¹⁹⁸. Knight¹⁹⁸ found that distinct active areas were present, each area adsorbing a particular type of group. Thus water improved the peak symmetry for alcohols but not for amines, and vice versa. The nature of the carrier gas itself may also affect the adsorbent and this is particularly pronounced for molecular sieves whose separating power for permanent gases is impaired by saturation with carbon dioxide.

Liquid modified adsorption columns separate paraffins and cycloparaffins on a carbon number basis^{83,84,296}, the selectivity being different from that of a liquid stationary phase. The polarity of adsorbent columns and, to a lesser extent, modified adsorbent columns is markedly affected by humidity^{84,161,165,262,288} and the preparation of reproducible adsorbents is difficult.

Molecular sieves have proven particularly useful for the separation of permanent gases and, at high temperatures, a wide range of hydrocarbons^{41,337}. Most straight chain organic compounds are strongly retained^{41,337}. Other adsorbents used include charcoal, silica gel and alumina (which irreversibly adsorbs carbon dioxide). Less effective adsorbents have been used for hydrocarbons up to C_7 and these include magnesium and aluminium silicates⁹, ethylene carbonate, bentonites³³⁵, kieselguhr and zeolites^{9,161}; in the case of charcoal and silica gel slow adsorption equilibrium has been reported¹³⁴.

Few satisfactory organic liquid phases have been found for high temperature operation^{5,61,89,99,116,187,252}. Those tried are relatively non-polar and include silicones, Apiezon M, polyethylene and polytrifluorochloroethylene¹⁸⁷, petroleum derived asphaltenes^{15,252}, polyesters and borazole derivatives⁹⁹. Generally preconditioning of the stationary phase is necessary at or above the operating temperature⁵⁰. On the other hand, it is found that thin liquid films have lower vapour pressures than the bulk liquid and column life is therefore longer than would normally be expected. For the separation of metals²⁹ and metal chlorides¹⁷⁷

inorganic chlorides have been used as liquid phases.

References to the large volume of published retention data, some of which has been collected in supplements to the *Journal of Chromatography*^{209,210}, are tabulated in Section 9. Most retention data have been published without consideration of the best column for a given type separation. However, some attention to this has been given in the case of methyl esters^{220,255}, phenols⁹¹, and hydrocarbons and oxygenated compounds^{17,320,306}. Keulemans¹⁹⁰ has also discussed the properties of various liquid phases and has pointed out that the large number of stationary phases used has made collection of retention data difficult. However, small differences between two phases can often be of importance. A smaller number of stationary phases can be used with columns of high efficiency and pure liquids with a definite chemical constitution should be chosen where possible. Mixed stationary phases generally give the same results as a series of separate columns^{233,265,161}.

The separation of metals²⁹, metal chlorides^{177,186}, deuterated cyclohexane³³⁸, and isotopes of neon¹⁰⁶ and of hydrogen^{97,245,299} are also of interest. Respiratory pigments have been used for the separation of nitrogen and oxygen¹⁰².

Aqueous samples are troublesome because of tailing of the water peak. Elvidge and Proctor⁸⁷ have determined water in pharmaceutical preparations over the range 30-80% on polyethylene glycol with good agreement with chemical methods and Smith²⁹⁷ has recommended columns for the analysis of various aqueous mixtures. Overlap of the water peak will not interfere with the determination of other components if a detector is used which is insensitive to water, e.g. the flame ionization or β -ray/nitrogen detectors.

5.2 Separation of complex mixtures

Multicomponent mixtures frequently contain components with similar and/or a wide range of partition co-efficients. These two possibilities will be considered separately but it should be noted that in both cases improvement results from the use of high efficiency columns.

Although simple mixtures can generally be resolved by appropriate selection of the stationary phase, the problem becomes more

complex as the number of components increases. Use of a series of stationary phases may then only reshuffle the peaks without allowing satisfactory resolution. This can be avoided by isolating sections of the chromatogram and transferring them to other columns. An example given by Simmons and Snyder²⁹⁸ is shown in Figure 5. Here the C_5 — C_8 fractions were separated on a carbon number

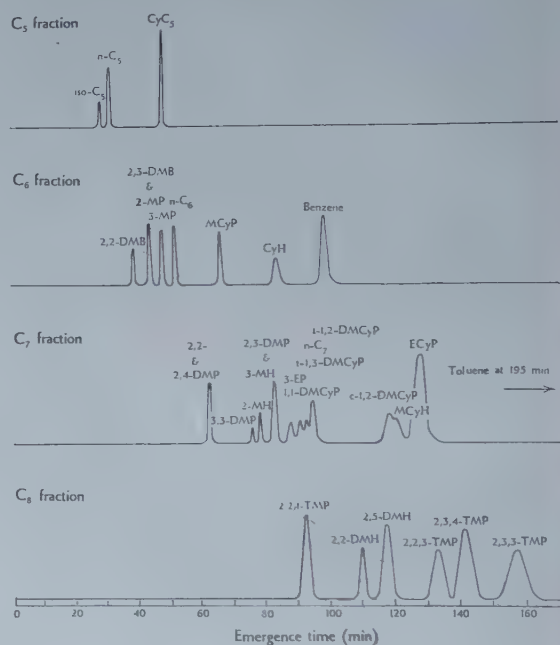


Figure 5 Two-stage separation of C_5 - C_8 hydrocarbons (courtesy of Analytical Chemistry²⁹⁸)

basis by a modified adsorption column and the fractions were then re-run on a silicone oil column. An interesting modification of the two-stage column has been reported by Smith *et al.*³⁰⁰. Carbon dioxide was separated from CO, NO and N_2 on silica gel and the CO was then converted to CO_2 with iodine pentoxide to separate it from NO and N_2 on a second silica gel column.

Molecular sieves are particularly useful^{41,337} for the selective adsorption of straight chain compounds although care is necessary to avoid secondary reactions between adsorbed compounds and those not normally retarded. They have been used⁴¹ for hydrocarbons up to C_{40} but some initial affinity for singly-branched hydrocarbons is found^{77,337}. A liquid phase of the molecular sieve type, tri-*o*-thymotide, has

recently been reported²³⁹. The fluorescent indicator liquid phase adsorption technique has been used^{27,84,336} for prior type separation of oxygenated and other polar compounds.

When a mixture contains components with a wide range of partition coefficients, the early peaks will be bunched together and poorly separated if the later peaks are to be recorded in a reasonable time on a single column. A multistage system, similar to the above, can be used for this case. A two-stage unit may employ either the same stationary phase at two temperatures¹²⁷ or two different stationary phases. Moreover, depending on the component distribution, the columns can be operated either in series^{127,142,240} or in parallel³⁹, or a combination of both by appropriate switching²⁹⁶. Strongly retarded unwanted components can be removed from the column by backflushing with carrier gas³²⁶.

The second method of dealing with wide range mixtures is to increase the column temperature or (used less frequently) the carrier gas flow rate during the chromatogram. Details of equipment for temperature programming have been published^{60,117,127}, and Habgood and Harris¹¹⁷ have shown that both the retention volume and temperature of a component can be calculated from isothermal data by graphical methods. This assumes a linear temperature rise but non-linear programming may give better separation of early peaks³¹². Straight line plots of retention time versus carbon number⁶¹ suggest that simple relationships to isothermal data can be derived. Chromatography, using a moving temperature gradient, also has possibilities for wide range mixtures but band mixing is difficult to avoid (see ref. 250).

There has been considerable interest in the relative merits of multistage equipment and temperature programming and an example of the results obtainable is shown in Figure 6. In general temperature programming will be more suitable for initial examination of a wide range mixture although two substantially different stationary phases should be tried in case peak overlap occurs. Multi-stage equipment is more versatile and is to be preferred for semi-automatic routine analyses where the necessary switching sequence can be preset, and retention time reproducibility is more easily attained.

Quantitative analysis with incompletely separated peaks has been discussed by Zhukhovitskii and Turkeltaub³⁴² and more recently by Grant and Vaughan¹¹². In the case of almost coincident peaks the peak shape, as measured by the ratio of positive to negative deflection of the first derivative of the curve, is very sensitive to the component concentrations at impurity levels of a few percent²³⁷. This derivative peak ratio method can therefore give quite accurate results in these cases.

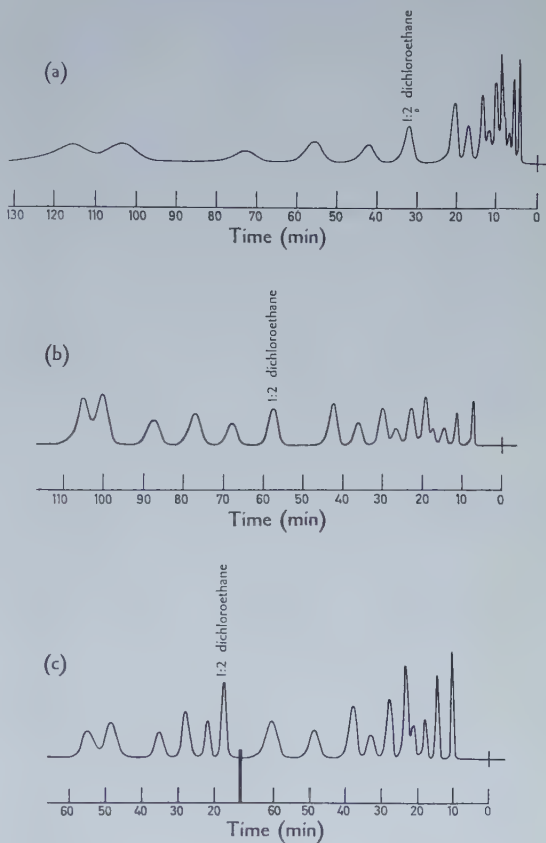


Figure 6 Comparison of two-stage and temperature programmed chromatograms (courtesy of Butterworth's Scientific Publications¹²⁷). (a) column temperature 75°C; (b) temperature programmed, 25 to 105°C; (c) two-stage analysis, 50 and 77°C

5.3 High speed analyses

The possibility of substantially decreasing analysis times has recently been investigated for both packed^{229,268} and capillary²⁹² columns and high speed chromatographs are already in

commercial production. High efficiency at high carrier gas flow rates results^{229,292} from the use of hydrogen or helium as carrier gas and of a low percentage of liquid phase on the support (see Section 3.2). According to Golay¹⁰⁸ optimum performance of a capillary column at the optimum carrier gas velocity (u_{min} in Figure 1) is obtained when the static phase capacity is just over 3 times the mobile phase capacity. However, Scott and Hazeldean²⁹² have shown that the ratio depends on the column and sample when the carrier gas velocity is well above the optimum value. For a specific case of a 0.02 in. i.d. capillary column they give a ratio of approximately 0.3.

A high speed analysis of a C₄ hydrocarbon mixture obtained with granular packed columns is no interference from peak overlap. In the duction and low detector and recorder time constants are necessary (see Section 3.5) for high speed analyses. In this case a specially designed gas sampling valve, described in Section 7, was used and a flame ionization detector unit with a time constant of 8 milliseconds was linked to an oscillographic recorder.

It has been pointed out²⁹¹ that cathode-ray presentation of chromatograms is cheaper than the use of a potentiometric recorder but if a permanent record is required oscillographic or potentiometric recorders may be more economical and more satisfactory in the long run. While oscillographic recorders will handle very fast records, a $\frac{1}{4}$ -second potentiometric recorder should be adequate for most purposes. Slower speed recorders can be used if the integral curve is recorded. Use of an "infinite persistence" oscilloscope allows a chromatogram to be examined at leisure without the accumulation of a vast amount of chart paper.

5.4 Identification of components

Where the components of a mixture are limited to only a few possibilities they can be identified by their retention characteristics (see Section 5.1). If this is not adequate, auxiliary analytical techniques are necessary. Suitable methods include mass spectrometry, infra-red and ultra-violet spectroscopy, electron affinity spectroscopy and chemical methods.

Fast response time-of-flight¹⁰⁷ or suitably

modified^{119,137} magnetic dispersion mass spectrometers are particularly suitable, but slower instruments can be used by stopping the carrier gas flow while the eluted component is analysed²⁶ without the need for collecting separate fractions. The recently introduced technique of electron affinity spectroscopy²²⁶ is also suitable for continuous analysis of small samples.

Separated fractions of a few milligrams can be identified by infra-red spectroscopy, either in the gaseous⁸, liquid³⁰⁸ or adsorbed³¹⁷ state. Specific chemical tests can also be used⁷⁹ and recently the methylene insertion reaction has been used²⁹⁵ to determine the structure of

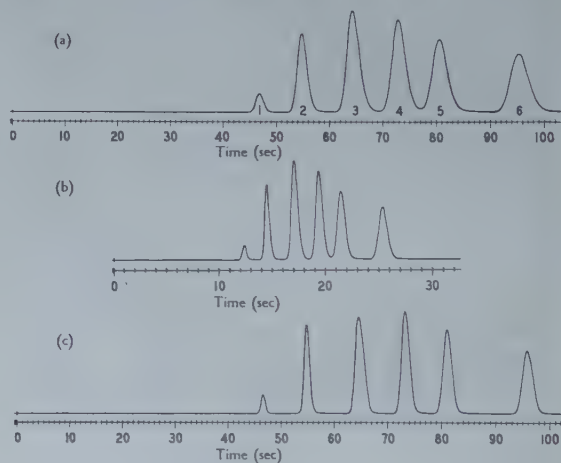


Figure 7 High speed chromatograms of C₄ hydrocarbons (courtesy of Analytical Chemistry²³⁰) (a) 4 ft column, nitrogen carrier gas; (b) 4 ft column, hydrogen carrier gas; (c) 12 ft column, hydrogen carrier gas. Sample components (1-6) i-butane, n-butane, butene-1 + i-butylene, trans butene-2, cis butene-2, butadiene-1,3

unknown hydrocarbons on a purely statistical basis.

In some cases the relationship between detector output and molecular parameters can also be used to identify a component, two separate detector signals being required if the weight of the component is unknown^{110,217,236}.

5.5 Analysis of non-volatile, reactive, and trace materials

Improved separation at lower temperatures can often be obtained by the conversion of materials to more volatile derivatives. Fatty acids are generally converted to the corres-

ponding methyl esters³¹⁰ and aminoacids to aldehydes³⁴⁹. Alcohols have been converted to acid esters²¹⁹, hydrocarbons⁷⁷ or nitrites⁷⁸, and phenols to methyl ethers⁴⁷ or trimethyl silyl ethers²⁰⁷.

Representative chromatograms can be obtained from the pyrolysis products of high molecular weight materials, and these show good reproducibility provided that the products are rapidly removed^{162,212,311}. This technique is particularly useful for the investigation and identification of polymers.

Reactive materials are sometimes converted to non-reactive derivatives, e.g. hydrogen chloride to carbon dioxide¹²⁶, but considerable progress has been made in the direct analysis of reactive samples^{86,145}. Contamination of the sample valve can be avoided by adding the sample continuously to the column downstream from the sampling valve. Injection of an air or inert gas sample into the carrier gas stream then gives a series of reversed peaks corresponding to the sample components. This technique may be regarded as a modified form of frontal analysis.

Trace components below the ppm level can be determined with milligram samples using high sensitivity detectors, providing that there is no interference from peak overlap. In the latter case, or with detectors of lower sensitivity, it may be necessary to remove the major component prior to analysis. Selective reagents have been used to remove aldehydes^{188,214}, olefins^{167,188,241,276}, esters, ketones and alcohols²¹⁴ and carbon dioxide³²³. Conversely the impurities can be concentrated on short adsorption or absorption columns^{40,88,332}, even with low pressure samples³²⁴.

5.6 Miscellaneous uses

Gas chromatography has been applied to a wide variety of analytical problems and a selection of examples is given below.

It has been used extensively for the analysis of biological materials, particularly for fatty acids, in studies of metabolism and the determination of alcohol content. Other complex materials investigated include essential oils and related products, flavours and perfumes and the components of cigarette smoke.

The majority of applications have been in the chemical and petroleum industries where

it is used for the control of raw material, intermediate and finished product quality and for the study of reactions and other analytical techniques, and also for the evaluation of exploratory oil well drillings and analysis of the combustion products of flames and internal combustion engines. It has also been used for the analysis of fuel gas, the atmospheres of coal mines, trace materials in nuclear reactor coolant gases, anaesthetics, aerosols and refrigerants, fractions from air rectification columns, printing ink volatiles and azeotropes, and for the selection of liquids for extractive distillation²⁷⁷, the controlling of water corrosion in tubes of high pressure boilers³⁵, the selective determination of alkoxy¹²⁸ and formyl and acetyl groups³⁰⁴ and in studies of sludge digestion and complex formation.

Other applications include the investigation of Henry's law, the determination of equilibrium and reaction rate constants, the study of catalysts^{120,318} and characterization of catalyst activity^{58,288} and the measurement of surface areas^{58,280}. Carbon/hydrogen ratios have also been determined^{81,314} by the use of gas chromatography.

6 PREPARATION OF PURE MATERIALS

Gas chromatography offers an excellent method for the preparation of highly pure materials and can be used for thermally unstable compounds. Analytical columns can generally be used only for relatively small samples of the order of 10 mg but if the components to be separated are well resolved the column can be considerably overloaded, and it has been reported that 0.3 ml samples have been separated on a 4 mm i.d. column. The preparation of larger amounts of material necessitates scaling up the equipment by increasing the column diameter and/or by repetitive injection and collection of samples, but in the latter case a saving in the amount of column packing material is achieved only at the expense of decreased sample throughput.

Increasing the column diameter has been found to result in loss in efficiency and Johns¹⁷¹ has reported that this effect is considerably pronounced above 0.7 in. diameter. He therefore used a series of $\frac{5}{8}$ in. diameter columns

in parallel to obtain the required column capacity without loss of efficiency. Recently this loss has been shown to be mainly due to the existence of a radial velocity distribution in the column^{109,143} which arises from uneven column packing and a high gas velocity near the wall. Some improvement can be made^{109,143} by constructing columns in short lengths interconnected by small mixing tubes and by roughening the column walls. An HETP of 1.3 mm has been obtained by collecting separately the effluents corresponding to the centre and wall sections of a 10 cm diameter column¹⁴³, and even without this refinement 3 in. and 10 in. diameter columns have given values of 2 mm and 2.5 mm respectively.

Because of the large carrier gas consumption of a preparative gas chromatograph, gas recycle after appropriate purification has been used in a commercial unit¹⁷¹. Another method, suggested by James¹⁴⁷, to overcome this problem is to use a condensable vapour as the carrier gas. On a very large scale the latter method would probably be essential because of the problem of pumping large volumes of dilute gas. So far hypersorption techniques, using a moving adsorbent bed²², have been regarded as more attractive.

When a large number of cycles is necessary for purification of the required amount of material, repetitive sample injection and collection is generally based on a preset time cycle¹¹. Sample collection can also be controlled automatically by the detector output^{132,204}. The repetitive injection of liquid samples contained in a reservoir can be done conveniently by application of gas pressure in a manner similar to that described by Heilbronner^{132,92}. Fischer and Brandes⁹⁰ have described a chromatograph to which the sample is added continuously but it operates, in effect, as a series of repetitive cycles.

Rapid vaporization of samples is necessary to prevent loss in column efficiency. Although vaporizers relying on heat capacity are often used, high-wattage on-demand vaporizers¹⁷¹ are more satisfactory for large samples. Metal capillaries heated by low-voltage current are excellent provided that the sample is injected uniformly into the column. To avoid thermal cracking of the collected materials by thermal conductivity detectors, and to avoid the large

gas flows, it is best to bypass a small part of the effluent through the detector and thence to waste; this technique also allows the use of other detectors which would destroy the sample.

One point to which particular attention must be given is the possible contamination of collected material by volatilization of either the liquid phase on the column or of its decomposition products^{99,116,195,334}. Insufficient heating of vapour transfer lines may also result in cross contamination of samples.

The collection of samples from a gas chromatograph is often complicated by supersaturation on cooling, which results in fog formation and entrainment of the solute. Klinkenberg¹⁹⁶ has suggested the following methods to prevent this — cooling in several steps, starting with a superheated vapour, using an adsorbent or absorbent, supplying extra heat while the gas is being cooled, and ensuring turbulent flow in the collector. Other methods employed include the use of electrostatic precipitators^{11,200} and the condensation of the emerging vapour after being mixed with a suitable solvent¹⁷⁵. Combined sample collection and scintillation detection has been described by Lowe and Moore²²⁷ who used a circulating liquid phosphor, and by Karmen and Tritch¹⁸² who used anthracene as both collector packing and scintillator.

7 PROCESS CONTROL BY GAS CHROMATOGRAPHY

Although gas chromatography generally produces only an intermittent analytical record, it has found wide application in process control. This has been due partly to the detailed direct information it gives and partly to the ease of maintenance and low down-time, of the order of 1%, and hence high reliability. In these respects the method is superior to both infra-red spectroscopy and mass spectrometry which it is replacing for many purposes. Moreover, with the recent development of high speed gas chromatographs (see Section 5.3), the instrument time lag has now been reduced in most cases considerably below that of the sampling system.

In common with other on-line analytical techniques, particular care is necessary in the installation of sampling lines and sample clean-

up equipment (see e.g., ref. 12) on which the ultimate accuracy depends. The problems related to the gas chromatograph itself are the selection of a suitable column, the reliable metering and introduction of samples to the column and the maintenance of long term stability with adequate sensitivity. In addition, the final results must be presented in an easily understood form.

The column selected must not only give adequate separation of the components of interest but must sustain its initial performance over an extended period. This is necessary to maintain adequate resolution and constancy of retention times for timer-controlled peak selection and for peak height measurement, both of which are usually employed. Partition columns must therefore be packed with a relatively non-volatile material which is not slowly eluted from the column, and many columns used for laboratory analyses are unsuitable for process instruments. Adsorption columns require close control of carrier gas humidity and must be protected from build-up of heavy organic components which would affect the column performance; liquid modified adsorbents are somewhat better in these respects. The use of multiple columns and back-flushing to remove unwanted heavy components is becoming standard practice on process control instruments. Long-term stability of retention times also involves close control of carrier gas flow rate and column temperature. The latter is usually controlled to within $\pm 0.1^\circ\text{C}$ on process instruments and heat is supplied either by direct electrical heating or by the circulation of heated air³⁰⁵.

A number of automatic gas sampling valves have been designed and these include the rotary type with flat sealing faces^{12,323} or with a floating plug³⁴³, the linear valve³⁰⁵ and the diaphragm valve¹⁷⁹. The latter most nearly approaches the ideal valve and one form is shown in Figure 8. It features simplicity of construction, low dead volume, high speed operation, freedom from leaks even under high pressure operation and an almost indefinite life. It has been reported¹⁷⁹ that a valve of this type still performed completely satisfactorily after 2 million cycles.

Unfortunately, liquid streams are more difficult to sample reproducibly than gas streams,

due to the very small volumes involved. It is usually the practice to vaporize the liquid sample and then to use a gas sampling valve. Vaporization of the sample without fractionation of the components may be achieved by passing it through a heated capillary tube.

Reliable quantitative data are dependent on reproducible detector response, adequate calibration and stability of the recorder baseline. Standard gas mixtures are generally employed to check the calibration periodically and appropriate adjustments can be made on this basis. Baseline drift of thermal conductivity detectors, especially when operating near their maximum sensitivity, is particularly troublesome. It has

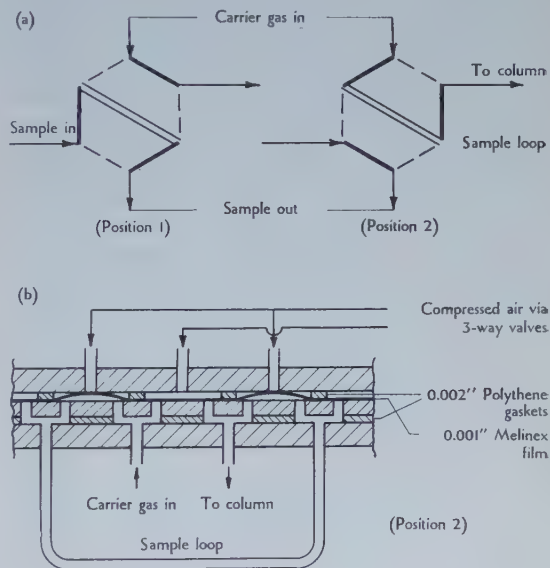


Figure 8 Diaphragm-type gas sampling valve. (a) diagrammatic; (b) sectional view (not to scale)

become standard practice to reset the bridge circuit automatically after each chromatogram has been recorded. Ionization detectors (see Section 8.3) offer a number of advantages over the thermal conductivity cell as they give more stable response over extended periods and much higher sensitivities with complete absence of baseline drift. Manufacturers of gas chromatographs have been slow to adopt ionization detectors for process control instruments but they will be necessary if high resolution capillary columns are to be used for process control.

It is generally not necessary to know the

concentrations of all components in a mixture. Selected peaks can be displayed in the form of a bar graph, thus conserving paper and leaving analysis trends visible for some time. However, although more expensive, multipoint presentation is clearer and is to be preferred. Print-out units are even more expensive and operate either on the basis of peak height or integrated area measurement. For automatic control, memory devices are necessary because of the intermittent data presentation, but few examples of direct control have been published.

Gas chromatography has been applied to the analysis of a wide range of organic process streams and also to inorganic analyses such as the determination of the hydrogen/nitrogen ratio in an ammonia synthesis plant¹² and for the measurement of chlorine purity³⁰⁵. An instrument which differs in a number of features from the usual process control gas chromatograph has been in use at the ICIANZ Ltd. polythene plant for about a year. This is equipped with a diaphragm-type sampling valve and a flame ionization detector (fully flameproofed) for the analysis of impurities in ethylene down to the part per million level. Sample size is only 0.3 ml. and the output has been presented on a logarithmic scale to avoid multiple attenuation changes for the different components.

8 APPARATUS FOR GAS CHROMATOGRAPHY

8.1 Sample introduction

The repetitive injection of gas samples has already been discussed in Section 7. The reproducible introduction of liquid samples is more difficult because of the small volumes involved. Methods which are commonly used include the capillary pipette system of Tenney and Harris³²¹ which is rapid and gives good reproducibility of milligram samples, the introduction of measured quantities of sample in thin glass capillaries which are subsequently broken^{36,231}, and the use of special hypodermic syringes. These include commercially available syringes of the Agla and Hamilton types^{46,315}. Injection valves designed to overcome leakage at high pressures have been described by Scott²⁹⁰ and by Samsel and Aldrich²⁸² and an

interesting liquid sampler has been described by Adams².

Volatile components can be stripped from a non-volatile material by a flow of inert gas either through the sample or over the sample distributed as a thin film on a supporting material. Solid samples must be added either in solution or in the liquid state⁵.

If an internal standard is used for quantitative analysis it is not necessary to add an exact amount of sample to the column, but more than one standard may be required for a sample with a wide range of component concentrations or elution times. Samples must be added evenly and without spreading to the column packing and additional heating of the sample inlet is generally required with liquid samples to ensure rapid vaporization (see e.g., ref. 261). When standard gas mixtures are made up in a gas blending apparatus (see e.g., ref. 123) correction must be made for non-ideality of the gases; correction factors for C₁ — C₅ hydrocarbons have been given by van de Craats⁵⁶.

The very small samples generally required for capillary columns can be added to the column by a sample division system⁷¹. This ensures rapid and reproducible introduction, and has so far shown no evidence of sample fractionation.

8.2 Columns and stationary phase supports

Granular packed columns are usually constructed of glass, stainless steel or copper, but other materials^{86,145} may be necessary with highly reactive samples. At high temperatures only glass may be satisfactory because of catalytic effects on the metal surfaces.

Liquid stationary phase supports are generally kieselguhr (*Celite*, *Chromosorb*) or crushed firebrick (*C-22*, *Sterchamol*). With regard to column efficiency it has been shown that there is little difference between narrow mesh fractions of *Celite* and *C-22*⁶⁷ but the firebricks are more adsorptive and may even result in isomerization or partial destruction of materials. Some improvement results from aqua regia washing^{253,348}, but even aqua regia washed *Celite*^{64,253} and *Chromosorb*⁶⁴ show tailing with polar samples when coated with a non-polar or slightly polar liquid. Residual

adsorptivity of the support may also result in retention times being dependent on the sample components.

Improved peak symmetry can be obtained by coating C-22 with a high percentage of silver²⁵³ or by adding a small percentage of a polar material to the support¹⁷⁰. Silicone coating of *Celite* with dichlorodimethylsilane has been used to prevent thermal decomposition of polyester stationary phases¹³⁹. A petroleum-ether washed detergent base gives good peak symmetry with pyridines⁶⁴ and with more basic nitrogen compounds on addition of 10% potassium hydroxide⁶⁵. Various inactive supports have been used (see ref. 125) to overcome peak asymmetry, but open supports are unsatisfactory due to low efficiency caused by molecular diffusion and supports of low macroporosity give low plate capacities (see Section 3.3). Microporous supports are unsuitable due to slow diffusion in the liquid phase.

Methods used for filling packed columns have been described by Keulemans¹⁹⁰, Rose²⁷⁹ and others²⁶⁴. Tapping the column after packing to consolidate the filling²⁶⁴ can sometimes give a column efficiency double that of a loosely packed column. Where possible the column should be vertical to prevent the possibility of channelling.

Capillary columns have been constructed⁷¹ of stainless steel, copper, gold, glass, and nylon²⁹². Best results have been obtained with glass columns⁷¹ and a hydrocarbon coating, and the high efficiency has been ascribed to the smoother internal surface of the glass capillaries. However, Zlatkis³⁴⁵ has reported that neither glass nor stainless steel coat as well as copper with polar liquids and also that nylon gives a poor coating. A device for drawing glass capillary tubing has been described by Desty *et al.*⁷³.

A variety of column heaters has been described and these employ either a circulating liquid or a vapour, or direct electrical heating of the column itself. The latter method is generally preferred for temperature programming since a low heat capacity can be achieved. Vapour heating gives the most uni-

form temperature distribution down the column but air circulation heaters are more flexible and convenient.

8.3 Detectors and data presentation

A considerable number of detectors have been developed for gas chromatography and their characteristics have been discussed in some detail in a previous paper²³⁸. Thermal conductivity has been used mainly in the past but ionization detectors are now being used to a greater extent. The latter offer considerably increased sensitivity and stability and lower time constants and dead volume. These points are particularly important for capillary columns, for which small samples and low gas flow rates are necessary, and in high-speed gas chromatography. Two ionization detectors have been used extensively for organic materials with both packed and capillary columns. These are the β -ray/argon detector developed by Lovelock^{224,225} and the flame ionization detector developed by McWilliam and Dewar²³⁸. For high sensitivity with most inorganic materials other detectors must be used^{135,181,260}.

Detector sensitivity is of particular importance and can best be expressed independently of column conditions in the form of the detection limit equivalent to the background noise. If the noise is measured on a peak to peak basis and includes 95% of all noise peaks (μ , see below), the probability of a noise peak exceeding twice this value, will be less than 1 in 10,000*.

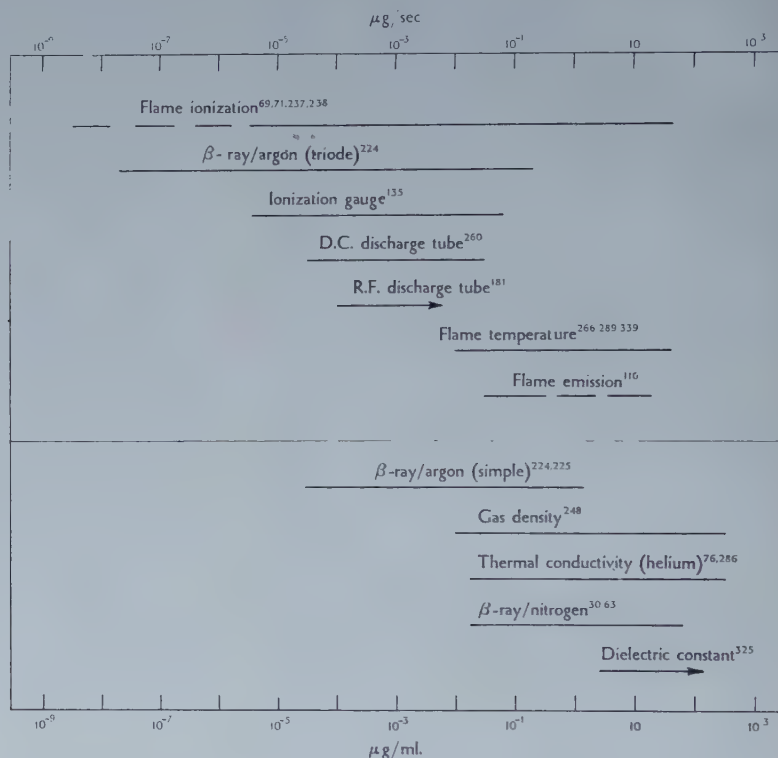
The detection limit should be given on a concentration basis ($\mu\text{g/ml.}$) when the signal output is unaffected by the gas flow rate as in the case of most non-destructive detectors, or on a time basis ($\mu\text{g/sec.}$) when the signal is proportional to the mass flow rate, e.g., for ionization detectors whose ionization efficiency is independent of flow rate. In the former case the peak height remains constant with change in carrier gas flow rate, in the latter case the peak area is constant. Detection limits obtained from published data are given for a number of detectors in Figure 9 together with the approximate linear ranges. The detection limit of thermal conductivity detectors is generally determined by temperature stability, whereas

*If the noise were of a single frequency, $f/2$, the probability of a noise peak exceeding the equivalent sample size μ/f with a base width of $1/f$ would be 4 in 10^{15} .

ionization detectors are virtually unaffected by temperature. However, it should be noted that the absolute sensitivity may still be affected by temperature, and figures given for the β -ray/argon detector²²⁵ show that a temperature stability of $\pm 0.8^\circ\text{C}$ is necessary for quantita-

molar percentages. More recently it has been shown that the response can be calculated on the basis of molar response within structurally similar homologous series, with an additional factor for the structural type^{222,244}. Present indications are that a similar scheme will be

Figure 9 Detection limits and linear ranges of various detectors (values obtained from references shown)



tive reproducibility of $\pm 1\%$ (the corresponding temperature stability required for the flame ionization detector is only $\pm 3^\circ\text{C}$ ²³⁷). The ultimate detection limit, μ_0 , of an ionization detector of the differential type which is limited by the statistical noise of the background ion current, I_0 , can be calculated from the equation given by Schiff and Evans²⁸⁴ for the expected fractional standard deviation of the ion current measurement. This leads to the expression

$$\mu_0 = 1.61 \times 10^{-8} (M/f_1)(I_0/2\tau)^{\frac{1}{2}} \mu\text{g/sec.} \quad (18)$$

In the case of the high sensitivity ionization detectors, μ_0 is generally determined in practice by the contribution to I_0 of the relatively volatile liquid "stationary" phases.

The response of thermal conductivity detectors using hydrogen or helium as carrier gas has been variously correlated with weight and

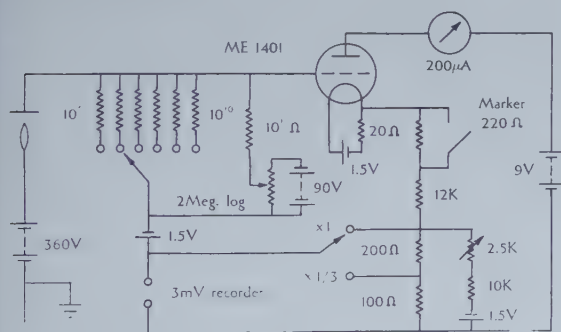
necessary for the β -ray/argon and flame ionization detectors in the low molecular weight region, the responses approaching a constant value on a weight basis (M/f_1 constant) at higher molecular weights. Relative response factors for thermal conductivity cells with nitrogen as carrier gas have been given by Jamieson¹⁷⁴⁶.

Most detectors at present in use are linear over a restricted range of about 1,000 to 1 (see Figure 9). For the determination of trace materials, high sensitivity detectors linear over a wider range are of great value since the impurities can often be measured by internal normalization on the main peak. Although the β -ray/argon detector is basically non-linear, the response can be made linear over a considerable range by use of a limiting resistor or by spacecharge effects²²⁴. The flame ionization detector has a basic linear response

chromatography, and both the β -ray/argon detector and the flame ionization detector are suitable for these applications. Detector time constants appear to be of the order of 10^{-3} sec. or less in each case² and the effective detector volumes are approximately $1\ \mu\text{l.}$ and less than $0.1\ \mu\text{l.}$ respectively. A small thermal conductivity cell with a volume of only $3\ \mu\text{l.}$ has been reported by Sasaki²⁸³ and fast response can be obtained²³⁶ by the use of fine wire or flake thermistors. Very rapid response can be obtained by varying the wire current to maintain a constant wire resistance. Peak distortion may also be caused by non-linearity of the detector response.

The problem of displaying a wide range of sample concentrations on a recorder of limited width is not confined to gas chromatography and scale multiplication systems commonly used for mass spectrometry are often employed. These include automatic range change devices operated by the recorder, either to return the pen to zero for the next range or by reversal of the recorder direction with change in sensitivity. The somewhat untidy chromatograms produced by the above methods and the necessity for range changing can be avoided by using a logarithmic or other non-linear scale.

Data processing systems to handle large numbers of samples have also been well developed for mass spectrometry. However, these are based on peak height measurements which may not always be satisfactory for gas chromatography where the peak area is the fundamental quantity. Various forms of integrators for automatic area measurement have been described, and these are based on either mechanical ball and disc integrators (which may be coupled to a pen-pipping system²⁵⁷ or a digital print-out unit¹²¹), their electrical equivalent¹¹⁸, integrating motors⁶² or a frequency shift system³².



Peak distortion resulting from detector volume and time constant has been discussed in Section 3.5. The restrictions are particularly stringent for capillary columns and high speed

9 INDEX TO RETENTION DATA

phases are given at the end of the table. Where only the number of stationary phases is given due to insufficient space, a complete list will be found under the reference number prior to the stationary phase abbreviations.

Compounds are listed in the order: 1 acetals,

acids; 2 alcohols; 3 aldehydes, ketones; 4 amines; 5 aromatics; 6 esters, methyl esters, methyl amino esters; 7 ethers; 8 paraffins and cycloparaffins, olefins and acetylenes; 9 phenols; 0 halogenated compounds, N-containing compounds (other than amines), S-containing compounds, miscellaneous compounds, non-hydrocarbon and light hydrocarbon gases.

The following abbreviations are used in addition to those for stationary phases (no symbol in column "d" implies (relative) retention time or volume): "b" log retention v. boiling point, "c" chromatogram

only, "C" log retention v. carbon number, "g" generally, "I" retention index (see Kovats^{199, 230}), "K" partition or activity coefficient, "I" log retention time, "T" log retention v. $1/T$, "TP" temperature programmed v. various, " V_g " retention volume per gram of stationary phase,* incomplete data for some phases or temperatures listed.

References 209 and 210 contain retention data from the following references: 209—3, 42, 43, 74, 111, 126, 146, 148, 150, 151, 153, 262, 313, 339 and 210—18, 23, 164, 185, 272.

No.	C. No.	No.	C. No.	1234567890	Stationary Phases	°C	d	ref.
<i>Acetals</i>								
6	3-6			23 678 0	HEGDE,ODPN	70		185
4	3-7			23 5678	(14)	g100		320
<i>Acids</i> (s-saturated only, u-unsaturated only)								
14*	s	1-12			DC550—stearic acid	100, 137		150
9	s	2-10			DC550—stearic acid	137		122
6	s	1-4		23456789	(6)	50, 100, 150		272
8		1-5			DOS—sebacic acid	150		273
<i>Alcohols</i> (a-aromatic incl., c-cyclic incl., p-primary only, s-primary and secondary only)								
8		1-5		3 6	DNP	80	c	274
8	s	1-5			BDP	79	c	147
11		1-6		3	Diglycerol,DNP	56?		192
8*	p	5-16		6	DC silicone grease	v,94-220		75
8*	s	1-5		56	DC702,TTP	30-80	T	223
4	p	1-4		3 6 8	Hyvac oil, TCP	25	1	214
17*		1-6		3 8	DIDP,Triol*	105	K	259
7		3-5		8	DIDP	v, 75-135	K	263
5	p	1-5		3 56 8	MPEG,PEG,PPG	100	V_g	3
8		1-5		1 3 5678	(14)	g100	b	320
5		1-4		3 6 8	Hexadecane	25, 40	K	205
18		1-8 (incl. glycols)		1 3456789	(6)	50, 100, 150		272
9		1-4		3 5678	PW,TTP	100		129
14		1-10		34	AL,Emulphor O	130, 70 or 190	I	199
15	acs	5-9		3 5678 0	AL,Emulphor O	130, 70 or 190	I	330
12	s	3-8		345 8	AL, Metal stearates	156		13
5	p	10-18			PEG monostearate	225	C	219
8		1-4		1 34 678	HEGDE,ODPN	70		185
6*		1-4		3 5678	DNP,PEG; Hyvac oil	70; 40	K	243
8		1-5		3 5678	(8)	100		287
7	s	1-5		3	Phenyl-naphthylamine	100		329
6	s	2-4			Armeen SD	88		341
10		4-7		345 8	Metal complexes	100 or 130	V_g	49
20		2-9		5 8 0	DOT-TTP,TOT-TTP	100		239
9*		2-8		3 5678 0	AL,BDP,DIN	75, 100, 150	V_g	44

Aldehydes, Ketones (a-aromatic incl., c-cyclic incl., m-methyl only, n-normal only, u-unsaturated incl.)

			9		2-7	2	6	DNP		78	c	274
			3		3-6	2		Diglycerol, DNP		56?		192
6	n	5-10						PW		150		75
3	n	2-4	3	m	4-5	2	6 8	Hyvac oil, TCP		25	l	214
			4		3-5	2	8	DIDP,SQ*,Triol*		105	K	259
			5		3-6	2	56 8	MPEG,PEG,PPG		100	V _g	3
8*		2-7						DC550,DCP,Pluronic F68,PW,TTP		110		130

No.	C. No.	No.	C. No.	1234567890	Stationary Phases	°C	μ	ref.		
4	n	2-5	5	m	3-7	12 5678	(14)	g100	b	320
2		2-3	3		3-5	2 6 8	Hexadecane	25, 40	K	205
4	u	3-4	6	c	3-6	12 456789	(6)	50, 100, 150		272
			4		2-6	2 5678	PW,TTP	100		129
			15		3-8		DNP	60-100	V _g	340
10	n	2-10				2 4	AL, Emulphor O	130, 70 or 190	I	199
5	a	7-8	37	ac	3-11	2 5678 0	AL, Emulphor O	130, 70 or 190	I	330
			7	c	3-7	2 45 8	AL, Metal stearates	156		13
6	u	2-4	5		3-5	12 678 0	HEGDE,ODPN	70		185
2*		2-3	4*		3-5	2 5678	DNP,PEG;Hyvac oil	70; 40	K	243
4	n	2-5	4		3-7	2 5678	(8)	100		287
			12	m	17-27	6	E301	265	C	249
			3		3-4	678	Dibutylphthalate	25		88
4		2-5				2	Phenylmaphthylamine	100		329
			6	cm	5-9	2 45 8	Metal complexes	100 or 130	V _g	49
4*	a	3-7	29*	c	3-9	2 45678	AL,BDP,DIN	75, 100, 150	V _g	44

Amines (a-aromatic incl., m-methyl only, p-primary only, s-primary and secondary only)

4	m	0-3					(7)	v, 65-100		153
27		1-12				0	Lubrol MO,PO	100		146
60*	a	6-11				0	BDP,Lubrol MO,PW	137		148
2	p	3-4				123 567890	(6)	50, 100, 150		272
18*	a	4-12				23 5 8 0	AL, Metal stearates	156	V _g	13
4	a	6-7				5 9	B34	200		141
10		2-9				23 5 8 0	Metal complexes	100 or 130	V _g	49
28	a	7-10				0	DC710	200		176

Aromatics

9*		6-11				2 6	DC702,TTP	30-80	T	223
6		6-8				8	BDP, Lubrol MO,PW;Octadecane	79; 65		152
17		6-9				8	DNP,MPEG,Nujol,PEG,PPG,TXP	120		42
24		12-20 (2 rings)					AM	197		20
5		6-9				23 6 8	MPEG,PEG,PPG	100	V _g	3
5		6-8				8	DNP,MS550,PO,TCP	100		111
6		6-8				8 0	BDP,Hexatriacontane	79		74
18		6-16 (1-4 rings)					DC silicone grease	g235		80
5		6-10				123 678	(18)	g100	b	320
4*		6-8				8	nC ₁₈ ,nC ₂₁ ,nC ₃₅ ,SQ	v, 30-135	K	205
7		6-8				1234 6789	(6)	50, 100, 150		272
6		6-8				23 678	PW,TTP	100		129
9		6-9					DOP	125		93
5		7-8					BDP,Benzoquinone,SQ,TTP	79	V _g	70
13*		24-36 (4-6 rings)					Polyphenyl tar	375, 430, 445		15
6		6-8					BDP;CIN,DMS,ECN	100; 50		348
51		7-12 (1-2 rings)					AL	150, 200		51
12		6-10				23 678 0	AL, Emulphor O	130, 70 or 190	I	330
3		8				4 9	B34	80		141
4		7-9				234 8	AL, Metal stearates	156		13
2*		6-7				23 678	DNP,PEG;Hyvac oil	70; 40	K	243
7		6-9				23 678	(8)	100		287
27*		6-14 (1-2 rings)				8 0	AL, Detergent	245	V _g	72
8		6-10				234 8	Metal complexes	100 or 130	V _g	49
5		6-8				2 8 0	DOT-TTP,TOT-TTP	100		239
41*		6-11 (1-2 rings)				23 678 0	AL, BDP, DIN	75, 100, 150	V _g	44

Esters (s-saturated only, u-unsaturated only; acid carbon numbers in brackets)

13	s	3-6 (1-4)				23	DNP	57	c	274
7	s	3-6 (1-4)				2 5	DC702,TTP	60-130	T	223

No.	C. No.	No.	C. No.	1234567890	Stationary Phases	°C	d	ref.
4	s	3-6 (2)		23 8	<i>Hyvac</i> oil, TCP	25	1	214
3	s	4-6 (2)		23 5 8	MPEG,PEG,PPG	100	V _g	3
14		2-6 (1-4)		123 78 0	HEGDE,ODPN	70		185
6	s	3-6 (1-2)		123 5 78	(14)	g100	b	320
4	s	3-5 (1-3)		23 8	Hexadecane	25, 40	K	205
23		2-10 (1-8)		12345 789	(6)	50, 100, 150		272
12	s	2-6 (1-4)		23 5 78	PW,TTP	100		129
6	s	7-13 (3)			Silicone oil (L 46)	220	c	322
50	s	2-9 (1-4)		23 5 78 0	AL, <i>Emulphor O</i>	130, 70 or 190	I	330
3		2-4 (1)		23 5 78	DNP,PEG	70	K	243
4		3-6 (2)		23 5 78	(8)	100		287
9	s	3-6 (1-2)		3 78	Dibutylphthalate	25		88
14		3-7 (1-5)			PEGA,DC550-stearic acid	80		271
22	u	4-14 (2-12)			(12 — mostly polyesters)	141		174
7	u	14-24 (12-22)			PEGA	250		174
11*	s	3-7 (1-6)		23 5 78 0	AL,BDP,DIN	75, 100	V _g	44

Esters—methyl (s-saturated only, u-unsaturated only; acid carbon numbers given)

5*	s	2-6		2	DC silicone grease	84, 100		75
5	s	10-18		2	DC silicone grease	218, 230		75
27		5-18			AM, <i>Lube oil extract</i>	197	151,	154
12	s	1-6			BDP,DOP,PW;DOP,PO	100; 79		151
8	s	6-20 (dicarboxy)			AM, <i>Lube oil extract</i>	197		154
9	s	6-18			DC silicone grease	150-250		251
8	s	3-10 (dicarboxy)			DC silicone grease	150-240		251
44	u	12-24			AM, <i>Reoplex</i>	197		309
12		8-22			<i>Reoplex</i>	240	V _g	254
9	s	18-34			E301	295		193
11		10-20			DC silicone grease, PEGA-PEGS	210	C	57
7	s	2-5 (mono, dicarb.)			DDP,DNS,DOA,PEG dioctanoate	150		270
4		4-8 (dicarboxy)			PEG dioctanoate, <i>Flexols</i> (2)	190		270
11		8-20			PEGS	210		287
36*		8-26			AL,PEGS, Silicone grease	g200	V _g	131
40*		5-22			AL;PEGA	197; 180		149
9	s	5-10		3	E301	150	C	249
11	s	15-25		3	E301	265	C	249
18		8-20			AL (capillary)	240		221
11		12-26			PEGS	203		220
14		8-22			<i>Reoplex</i>	200		255
16*		16-20			AN;PBS,PEGA, <i>Reoplex</i>	270; 225		140

Esters—methyl amino-

8*		3-9			Silicone oil — Na capronate	v	c	19
8		2-6			DC550	TP	c	215

Ethers (a-aromatic incl., am-arylmethyl, c-cyclic incl.)

4		4-8		123 56 8	(14)	g100	b	320
3	c	4-6		123456 89	(6)	50, 100, 150		272
12	am	7-9			AM	145		47
15	a	9-12 (trimethylsilyl)			DBTCP,DC550	125	V _g	207
5	c	4-8		23 56 8	PW,TTP	100		129
21	am	7-10		4 90	(5)	v, 140-190		91
7	a	4-10		23 56 8 0	AL, <i>Emulphor O</i>	130, 70 or 190	I	330
5		2-8		123 6 8 0	HEGDE,ODPN	70		185
4*		2-6		23 56 8	DNP,PEG; <i>Hyvac</i> oil	70; 40	K	243
3		4-8		23 56 8	(8)	100		287
2		4-6		3 6 8	Dibutylphthalate	25		88
15*	ac	4-10		23 56 8 0	AL,BDP,DIN	75, 100, 150	V _g	44

No.	C. No.	No.	C. No.	1234567890	Stationary Phases	°C	d	ref.
<i>Paraffins and Cycloparaffins, Olefins and Acetylenes (a-acetylenes incl., c-cyclic incl., n-normal only)</i>								
7*	c	1-5	4*	a	2-4	Charcoal, Silica gel	20, 80	158
5	c	1-4	9	a	2-4	AA, Ag-Glycol, Triisobutylene	20	37
11	c	5-7				DOP	65	218
43	c	5-10	13*		5-8	BDP, Lubrol MO, PW; Octadecane*	79; 65	152
6	c	6-10	7	c	6-10	DNP, MPEG, Nujol, PEG, PPG, TXP	120	42
5		1-4	5	a	2-3	Charcoal, Silica gel	20, 80	V _g 160
7		1-5	15	a	2-5	DMS; DIDP	0; 35	94
3	c	5-6	3	c	5-6	1.5% SQ-P	40	84
5		6	17		6	DDP, DTFP	20	313
7	c	3-7			23 6	Hyvac oil, TCP	25	l 214
14	c	5-9	3		6-8	DIDP, SQ*, Triol*	105	K 259
8	c	5-9				DIDP, SQ*	v, 75-135	K 263
11*	c	1-6	6*		2-4	(6)	v, 0-100	246
5	n	5-10				MPEG, PEG, PPG	100	V _g 3
7	c	3-6	17		3-5	Methyl Carbitol, DMS	0	339
9*	c	2-7	6*	a	2-4	(9)	20, 80	V _g 161
4	n	6-10				DNP, MS550, PO, TCP	100	111
7*	c	2-5	18*	a	2-5	DMF; DNP	0; 40	319
61	c	4-10	14	c	5-8	BDP, Hexatriacontane	79	74
19	c	5-10	21	ac	5-9	(18)	g100	b 320
4*	c	5-6	7*	c	5-6	(7)	25	K 197
25	c	5-7				ODPN, 3% SQ; 1.5% SQ-P	25; 75	c 82
27	c	5-10				PW; 1.5% SQ-P	150; 100	296
9*	c	5-7				SQ-IQ, Quinoline-brucine	25	c 344
7		2-5	7		2-4	DMS	0	V _g 303
4	c	5-6				Hexadecane	25, 40	K 205
14*	c	4-8	4*		6-8	nC ₁₀ , nC ₁₈ , nC ₂₄ , nC ₃₅ , SQ, TCB	v, 30-135	K 205
10		4-8				(6)	50, 100, 150	272
7	c	5-8				PW, TTP	100	129
21	c	5-12	18	c	5-9	AL, Emulphor O	130, 70 or 190	330
8		6-12				AL, Metal stearates	156	13
5	c	6-10				HEGDE, ODPN	70	185
10*		2-7				DNP, PEG; Hyvac oil	70; 40	K 243
6		2-5	7	a	2-4	DMS	0	98
8*	c	2-5	14*	a	2-5	AA, Decalin	21	l 138
			12*		2-8	Ag-Glycerin, Ag-Glycol	50	21
19*	c	1-8	18	a	2-6	(8), DMS (50° only)	50, 100	287
23	c	1-7				α-naphthylamine	50	c 190
			11		10-22	AL	221, 240, 256	C 219
7		1-5	8	a	2-4	Alumina-water or silicone oil	16	288
6		2-5	6		2-4	DBT, DMF, MS, Alusil	20	167
			8	c	6-7	Ag-Glycol	30	294
			4	c	7	Ag-Glycol	30	101
6	c	4-7	23	ac	2-5	Ag-Benzylcyanide, DMS	15, 20, 35	V _g 10
3		1-3	3		2-3	Silica gel	50	96
27*	c	2-9	22*		3-7	Dibenzyl ether, DBM, DC550	46	142
4		3-4	5		4	DMS, ODPN, Tetradecane, TTP	25	c 346
35	c	4-10				Dibutylphthalate	25	88
33*	c	2-7				13% IQ, 3% CIN	—	c 242
55*	c	5-24				AL, Detergent	245	V _g 72
			5		4	PC-GN	23	c 235
12		2-7	16	a	2-6	Hexamethylphosphoramide	0, 20, 35	V _g 232
15		17-27				E301	220	C 77
24*	c	1-7	67*	ac	2-7	DDP, DMS, ODPN, PO, TTP	v, 25-55	136
5		4-6	10		4-6	IQ	25	136
4		8-11	4	n	8-11	Metal complexes	100 or 130	V _g 49

No.	C. No.	No.	C. No.	1234567890	Stationary Phases	°C	d	ref.
10	c	6-14	5	7-12 2 5 0	DOT-TTP,TOT-TTP	100		239
32*	c	5-14	24*	c 5-14 23 567 0	AL,BDP,DIN	75, 100, 150	V _g	44
<i>Phenols</i>								
36		6-10			DDP,DC silicone grease	g150		23
30		6-10			AL	135, 155, 183	V _g	144
4		6-8		12345678	(6)	50, 100, 150		272
17		6-9			DOP	160		183
47		7-15		7 0	AL,DDPS, Detergent	150-250	V _g	91
13*		7-10		7	(15 — see reference)	v, 140-190	V _g	91
12*		6-9 (dihydric)		7	AM; E301	190; 180		91
13		6-8			MS-DNS	175		301
19*		6-10			(15 — mainly sugars)	v, 150-190	V _g	164
13*		6-14 (dihydric)			(6 — see reference)	v, 190-230	V _g	168
24		6-9			AL, Silicone grease	165		203
4		6		45	B34	200		141
<i>Halogenated compounds (a-aromatic incl., c-cyclic incl.)</i>								
8		1-5 (1I)			PW	100	c	147
18		1-2 (1-5Cl)			PO	100		14
23*	a	6-8 (0-1I,Br,0-2F,Cl) amines			BDP,Lubrol MO,PW	137		148
9*		1-2 (0-2F,0-3Cl)			Charcoal, Silica gel	80	V _g	160
6		0-3 (1-4Cl) silanes			Nitrobenzene	25		95
10*		1 (0-3F,0-3Cl)			(8)	v, 20-137	V _g	262
26		1-5 (1-4Cl)			DNP,MS710,PO,TCP	35, 77		126
6		1-2 (1-4F,0-3Cl)			Hexadecane	20?	c	278
15		1-3 (1-4Cl)			HEGDE,ODPN	70		185
9		1-3 (1-4Cl)			(6)	50, 100, 150		272
23		2-6 (1-2Br)			Silicone oil, Tween 60	TP	b	233
11*		6-7 (1-3Cl) phenols, anisoles			AL,BDP,DC703,DDPS,Zn stearate	g190		91
4		4 (1 Cl)			DIDP	65, 85		328
22		1-6 (0-1Br,0-4Cl)			AL,Emulphor O	130, 70 or 190	I	199
19	ac	5-8 (0-1I,Br,F,0-2Cl)			AL,Emulphor O	130, 70 or 190	I	330
12		1-3 (1-4Cl)			PW	90		328
18*		1-2 (0-3Br,0-4Cl)			DNP,Glycerol,Silicone 702	v, 20-100	K	124
3		1 (2-4Cl)			Water	v, 23-27	K	124
5		1-2 (3-6Cl)			DOT-TTP,TOT-TTP	100		239
<i>N-containing compounds (a-aromatic incl., c-cyclic incl.)</i>								
6		5-8 pyridines			DC550,Lubrol MO,PO	137		146
16		5-8 pyridines			(6)	g120		43
8		phosphonitrilic chlorides			E301	205	—	103
21	a	7-9 aromatic nitro-			DC710	200		176
7		8-20 nitriles			PEG monostearate	226	C	219
14		tobacco alkaloids			PBG,PEG,PPG	g190		269
8		nitroparaffins			AT,Lubriseal,Wemco C	97 or 128		25
7	a	2-8 nitriles			AL,Emulphor O	130, 190 or 70	I	330
9	ac	1-7 nitro-			AL,Emulphor O	130, 190 or 70	I	330
8		1-5 nitrites			DC silicone grease	70 or 100		78
15		5-9 pyridines			(11)	130	V _g	64
4		2-4 nitriles			PEG; Polyester succinate	70; 100		230
6		5-7 pyridines			Metal complexes	100 or 130		49
4*	a	2-7 nitriles			AL,BDP,DIN	75, 100	V _g	44
5*		4-7 pyrroles			AL,BDP,DIN	75, 100	V _g	44
<i>S-containing compounds (m-mercaptans, s-sulphides, t-thiophenes)</i>								
7	st	3-6			BDP, Hexatriacontane	79		74
8	mst	0-4			TCP	TP	c	281

No.	C. No.	No.	C. No. 1234567890	Stationary Phases	°C	d	ref.
24	mst	3-7		TCP	v, 65-101		6
17	ms	1-7		DNP	50	V _g	302
16	s	2-10	di-,trisulphides	AM,PEG, <i>Reoplex</i>	150	V _g	48
11	mt	3-5		IDPN, White oil	84		180
23	mt	2-10		SQ	TP		312
38	st	5-11		Detergent	245	V _g	72
9*	st	4-7		AL,BDP,DIN	75, 100	V _g	44

Miscellaneous compounds

4	4-9	peroxides	DNP	78		1
5	10	terpenes	PEG	177		24
4	0	boron hydrides (2-5B)	PO	27	c	184
21		terpenes, related comps.	Silicone grease-capronates	160, 187		18
5	9-10	methyl glycopyranosides	AM	170		234
21		ester-type plasticisers	<i>Apiezon oil K</i>	283		213
10	7-14	antioxidants	PPG, Silicone	200		169
11	10	terpenes	DC550,TCP	100	V _g	216
6	2-4	oxides	HEGDE,ODPN	70		185
8	6-14	pesticides	DC silicone grease	240		54
21		silanes (1-8Si)	<i>Silicone 702</i>	110	V _g	33
8	10	terpenes	AM	122		333
41	10-36	natural products	4%AL	v, 100-228		85
7	13-14	ionones, methylionones	AL	180 or 195		59
6	3-12	diboranes (1-2B)	PO	60-100	V _g	293
4*	0	metal chlorides	Octadecane,SQ	100, 150, 200	V _g	186
10	g10	mint oil constituents	PEGA,SAIB	120, 145, 170	V _g	298

Non-hydrocarbon and light hydrocarbon gases (p-method of preparing stationary phase described)

H ₂ ,CH ₄ ,CO ₂ ,C ₂ H ₆ ,C ₂ H ₂	carrier gas — N ₂	Charcoal	40	c	275
H ₂ ,N ₂ ,CH ₄	CO ₂	Charcoal (p)	20		157
CH ₄ ,C ₂ H ₆ ,C ₃ H ₈	CO ₂	Silica gel (p)	20		157
H ₂ ,N ₂ ,O ₂ ,CO,C ₁ -C ₅ (10)	CO ₂	Charcoal, Silica gel*	20, 85*		158
He,Ne,A,Kr,Xe	CO ₂	Charcoal	20		159
A,N ₂ O,NO,CO,Kr,Xe,C ₁ -C ₃ (5)	CO ₂	Charcoal (p)	20	V _g	161
Cl ₂ ,Br ₂ ,I ₂	N ₂ ,CO ₂	Silica gel (p)	v, 14-120	V _g	166
H ₂ ,O ₂ ,N ₂ ,CH ₄ ,CO	He	Molec. sieve 5A (p)	100	c	206
O ₂ ,N ₂ ,NO,CO,CO ₂ ,N ₂ O	He	Silica gel (p)	v		316
N ₂ ,ClF,HF,Cl ₂ ,ClF ₃ ,Br ₂ ,BrF ₃ ,UF ₆	A	<i>Kel-F</i> on PTFE	48		86
A,O ₂ ,N ₂	N ₂ ,H ₂	Molec. sieve 5A (p)	18		327
N ₂ ,NO	H ₂	Molec. sieve 5A (p)	86	c	211
H ₂ ,O ₂ ,N ₂ ,CH ₄ ,CO	A,H ₂	Calcium zeolite (p)	22	V _g	165
He,Ne,H ₂ ,O ₂ ,N ₂	A	Molec. sieve 5A	20	V _g	202
N ₂ ,Kr,CH ₄	H ₂	Charcoal, Molec. sieve 5A	20	V _g	202
He,Ne,H ₂ ,O ₂ ,A,Kr,Xe,CH ₄	v.	Charcoal, Silica gel, 5A	v.		113
He,Ne,H ₂ ,N ₂ ,O ₂	A	Molec. sieve 5A	22	V _g	201
A,O ₂ ,N ₂	He	Molec. sieve 5A (p)	v	c	208

Stationary phases not listed in table: 43—glycerol, *Nujol*, PEG, *Silicone M430*, triethanolamine, *TXP*; 64—AL,DC703, DC silicone grease, *Detergent*, diphenylphthalate, monohydroxyethyltrihydroxypropyl-ethylenediamine, *Octoil*, *Octoil-S*, PO, SQ, TCP; 91—AL, BDP, *Detergent*, glycerylmonostearate, *Paraplex G-50*; 153—DC550-Hendecanol, glycerol, Hendecanol, Hendecanol-PO, PO; 161—charcoal, di-

butylphthalate, dimethylaniline, DNP (all on zeolite), *Glauconite*, *Zeolites* (Ag, Mn, Na); 197—DIDP, DMS, glycol, ODPN, SQ, SQ-P, *Triol*; 246—alumina-2% silicone oil, benzylbenzoate, diethylformamide-silicone oil, DMF, vacuum pump oil-hexamethylphosphoramide; 262—charcoal, dibutylphthalate, DNP, glycerol, PO, *Silicones 702* and *1107*, water; 272—DC200, DDP, diethylhexylseba-

cate, fluorene-picric acid, PEG, tetraethyleneglycoldimethylether; 287—AL, DC200, DC silicone grease, DDP, diethylhexylsebacate, DIDP, PEG, PEGS; 320—(AL), *Convachlor-12*, *Convoil-20*, DC703, *Deergent*, diphenylformamide, ethylhexylsebacate, (*Fluorolube-S*), IDPN, ODPN, (perfluorotributylamine), *Polyglycols 166-450* and *174-500*, PPG, (SQ), thiodipropionitrile, TCP.

Stationary phase abbreviations: AA—acetonilacetone; AL, AM, AT—*Apiezon* greases; BDP—benzyl-diphenyl; CIN—chloronaphthalene; DBM—dibutylmaleate; DBT—dibutyltetradecane; DBTCP—dibutyltetrachlorophthalate; DCP—dicaprylphthalate; DDP—didecylphthalate; DDPS—diaminodiphenylsulphone; DIDP—diisodecylphthalate; DIN—dioctylester of dinitrodiphenic acid; DMF—dimethylforma-

mid; DMS—dimethylsulpholane; DNP—dinonylphthalate; DNS—dinonylsebacate; DOA—dioctyladipate; DOP—dioctylphthalate; DOS—dioctylsebacate; DOT—di-*o*-thymotide; DTFP—ditetrahydrofurfurylphthalate; ECN—ethylene carbonate nitronaphthalene; HEGDE—hexaethylene glycoldimethylether; IDPN—iminodipropionitrile; IQ—isoquinoline; MPEG—methoxy PEG; MS-DNS—methyl silicone oil-dinaphthylsulphone; ODPN—oxydipropionitrile; PBG—poly butyleneglycol; PBS—poly butylenesuccinate; PC-GN—propylene carbonate-glutaronitrile; PEG—poly ethyleneglycol; PEGA—PEG adipate; PEGS—poly diethyleneglycolsuccinate; PO—paraffin oil; PPG—poly propyleneglycol; PW—paraffin wax; SAIB—sucrose acetate isobutyrate; SQ-P—squalane-*Pelletex*; TCB—trichlorobenzene; TCP—tricresyl phosphate; TOT—tri-*o*-thymotide; TTP—tritolyolphosphate; TXP—trixylenylphosphate.

10 SYMBOLS USED IN TEXT

A, B, C	constants in HETP equation.	V_L	volume of liquid stationary phase in column $= nv_L$.
a, b	constants.	V_M	gas holdup of column and detector assembly.
C_1, c_2	"peak height" concentrations of sample components.	V_N	net retention volume $= jV_R'$.
f^0	fugacity.	V_R	uncorrected retention volume (also V_1, V_2).
f_i	fraction of molecules ionized.	V_R'	adjusted retention volume $= V_R - V_M$.
GLC	gas-liquid chromatography.	v_G	interstitial column volume per theoretical plate.
GSC	gas-solid chromatography.	v_L	liquid phase volume per theoretical plate.
H	height equivalent to a theoretical plate (HETP)	v_{eff}	effective plate capacity $= v_G + Kv_L$.
I_0	background current of ionization detector.	α	separation factor $= (V_R')_2/(V_R')_1 = K_2/K_1$.
j	pressure gradient correction factor.	γ_t, γ_p	activity coefficients (γ_t^0, γ_p^0 at infinite dilution)
K	partition (or adsorption) coefficient.	ΔG	free energy of solution.
k'	ratio of fixed phase to moving phase capacity $= Kv_L/v_G$.	ΔH_A	heat of adsorption.
M	molecular weight.	ΔH_S	apparent heat of solution.
M_L	moles of liquid stationary phase per unit volume.	ΔH_S^E	excess partial heat of solution.
m_1, m_2	molar quantities of components 1 and 2.	ΔH_v	heat of vaporization.
N, N'	carbon numbers of solute and solvent.	ΔS	entropy of solution.
n	total number of theoretical plates.	η	fractional band impurity.
p^0	vapour pressure of pure liquid.	μ	detection limit based on 95% of noise peaks ($\mu g/ml$ or $\mu g/sec$).
R	gas constant.	σ	standard deviation.
r	apparent retention ratio $= (V_R)_2/(V_R)_1$.	τ	time constant of detector and associated equipment.
T	absolute temperature.		
u	linear carrier gas velocity.		

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